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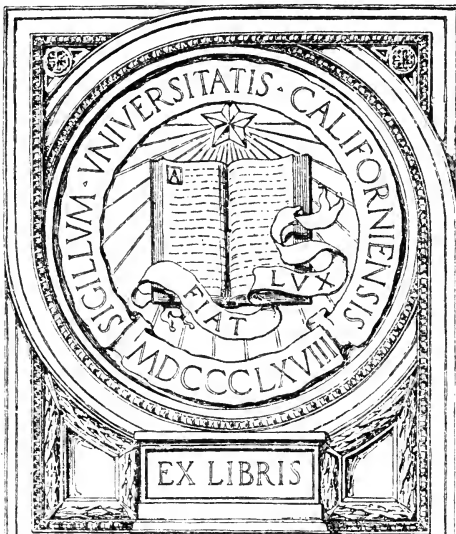
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GUIDE
TO
PREPARATION WORK
IN
INORGANIC CHEMISTRY
FOR
STUDENTS OF
CHEMISTRY AND PHARMACY

BY
DR. REINHART BLOCHMANN
Professor at the University of Königsberg

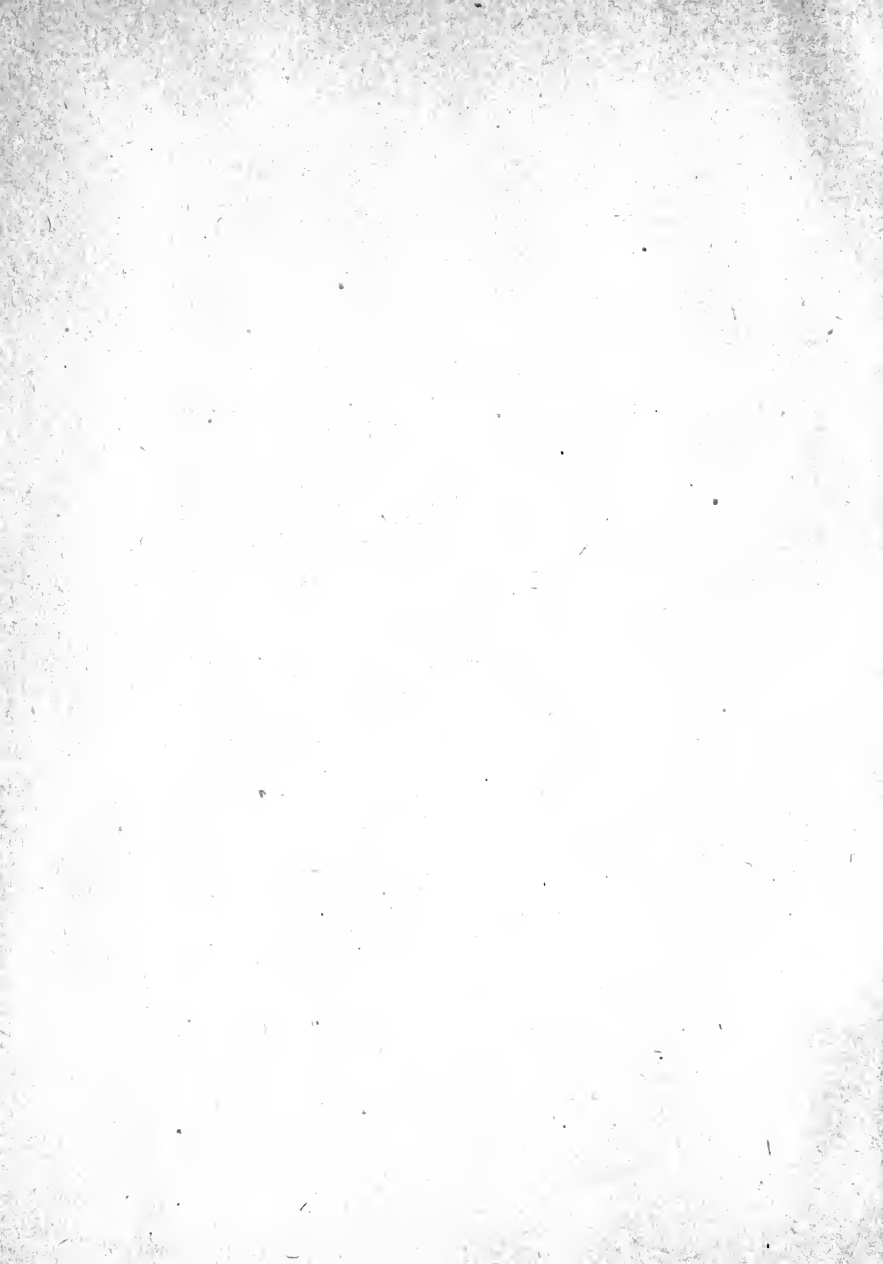
With Numerous Illustrations

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AUTHORIZED TRANSLATION BY
JAS. LEWIS HOWE
Washington and Lee University

DEPARTMENT OF CHEMISTRY
WASHINGTON AND LEE UNIVERSITY
LEXINGTON VIRGINIA



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P R E F A C E .

This little book is intended to serve as a first guide to students of chemistry and pharmacy in inorganic preparation work; it assumes that by practical work the student has already acquired a good knowledge of analytical chemistry.

The rational preparation of chemical compounds must *always* rest upon the stoichiometric proportions of the reacting substances. The course of the reaction is given briefly under each preparation and then a definite exercise is assigned. The quantities of all the materials used are to be determined and weighed by the student himself. Where on practical grounds, or for other reason, a departure from the stoichiometric quantities seems to be demanded, attention is called to it and the reason sought. Hence the student cannot avoid a careful quantitative study of those chemical processes which he carries out.

The amount of substance which can be obtained, or the ratio in which this stands to the theoretical, is given, for comparison with the results obtained by the student. It is here assumed that the process is carried out to completion. Wherever it has seemed necessary, attention has been called to the indications by which the end of the operation may be recognized, and also to the various phenomena during the reaction, which serve as a guide for its proper course.

When it is intended to prepare a certain compound, this can be accomplished, in very few cases, by the direct union of the materials involved (as in case of the action of ferrous sulfate, sulfuric acid, ammonia and nitric acid to form iron alum), without the formation of by-products. In most cases by-products are formed; indeed, certain branches of chemical industry are

industrially possible only on account of the value of these by-products. In all cases where by-products of value are formed, the recovery of these in useful form is carried out, in order that the student may early become accustomed to the consideration of a reaction from every standpoint.

In the selection of preparations three points have been taken into account:

1. As raw materials are used,
 - (a) Natural products such as barite, cryolite, stibnite, etc., or products of the larger chemical industries, as sulfuric acid, hydrochloric acid, soda, saltpeter, etc.;
 - (b) The chief products or the by-products of the previous preparations.

The cost of the raw materials for carrying out this preparation work is, therefore, low,¹ and the preparation of large quantities of worthless material is avoided.

2. The length of time which the single operations require without interruption rarely exceeds an ordinary laboratory period of two or three hours.

The statement of the time in each case renders possible the best disposition of it by the student.

3. The preparations have been so chosen as to give opportunity for the student to become acquainted with the most varied chemical processes, the most frequently used operations, and many easily prepared and approved forms of apparatus.

As regards the presentation of the subject, under each preparation is first given a list of the necessary raw materials, next a short sketch of the course of the chemical reactions involved,

¹ The cost of the raw materials for carrying out all the preparations given in this book is about \$1.50.

and then the exercise is definitely stated. The description of the method of carrying out the operation and of setting up the apparatus to be used, is given in the earlier preparations with great fulness. In the later exercises, assuming an acquired facility, the descriptions are much briefer. A paragraph as to the amount of the product, its properties and tests, concludes each section.

R. BLOCHMANN.

Königsberg, January, 1895.

For several years Blochmann's *Anleitung zur Darstellung chemischer anorganischer Präparate* has been used in my classes and has fully demonstrated its value.

The translation is made from a copy specially corrected and annotated by the author.

J. L. H.

*Washington and Lee University,
Lexington, Va., August, 1902.*

CONTENTS.

PREPARATIONS.

1.	Hydrochloric Acid.....	3
2.	Ammonia.....	7
3.	Sodium Ammonium Sulfate.....	11
4.	Nitric Acid.....	12
5.	Fuming Nitric Acid.....	14
6.	Soda and Alumina from Cryolite.....	16
7.	Alum.....	18
8.	Silver Nitrate from Coin Silver.....	19
9.	Liquid Sulfur Dioxid.....	21
	A. Precipitation of Copper from Copper Sulfate.....	22
	B. Preparation and Condensation of Sulfur Dioxid.....	23
10.	Iron Ammonium Alum.....	27
11.	Potassium Nitrite.....	29
12.	Phosphoric Acid.....	32
13.	Disodium Phosphate, Sodium Ammonium Phosphate, Pyrophosphoric Acid and Metaphosphoric Acid.....	35
	A. Disodium Phosphate.....	35
	B. Sodium Ammonium Phosphate.....	36
	C. Pyrophosphoric Acid.....	36
	D. Metaphosphoric Acid.....	37
14.	Lead Peroxid.....	38
15.	Antimony Trichlorid.....	40
16.	Fluosilicic Acid.....	43
17.	Crystallized Silicon.....	46
18.	Recovery of Tin from Tinsplate.....	47
19.	Carbamid (Urea).....	49
20.	Barium Nitrate.....	51

21.	Hydrated Barium Peroxid.....	52
22.	Hydroxylamin Hydrochlorid.....	55
23.	Phosphorus Pentachlorid	57
24.	Monochlorosulfuric Acid.....	59
25.	Amidosulfonic Acid.....	61
	A. From Monochlorosulfuric Acid.....	61
	B. From Hydroxylamin.....	64

TABLES.

Atomic Weights and Multiples.....	69
Specific Gravity of Hydrochloric Acid.....	70
Specific Gravity of Nitric Acid.....	70
Specific Gravity of Concentrated Sulfuric Acid.....	71
Specific Gravity of Aqueous Ammonia.....	71
Solubility of Certain Salts (in 100 parts water).....	72
Solubility of Certain Salts (water required for 1 part).....	73

PREPARATIONS

1. Hydrochloric Acid.

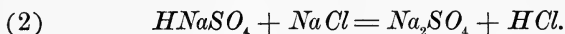
(By-product: *Hydrogen sodium sulfate.*)

Raw Materials: Common salt, concentrated sulfuric acid, concentrated hydrochloric acid (commercial).

By the action of concentrated sulfuric acid on common salt at ordinary temperature or at moderate heat, hydrogen sodium sulfate is formed, in addition to the hydrochloric acid, and this is the case even when the salt is in excess:



It is only at high temperatures that the hydrogen sodium sulfate reacts with the excess of sodium chlorid, according to the reaction:



On a small scale¹ hydrochloric acid is prepared according to the reaction:



Exercise: To prepare 500 grams of aqueous solution of hydrochloric acid containing 20 per cent. of HCl.

The apparatus (see Fig. 1) consists of a flask *A*, which rests on a sand bath; a wash bottle *B*; a retort *C*, which contains the water in which the hydrochloric acid is absorbed. The retort stands with its body in a dish holding about 3 liters, and is held by the clamp of a retort stand loosely, so that it can be rotated about the axis of its neck.

The flask *A* is round-bottomed, holding about 2 liters. Its mouth is

¹ On a large scale hydrochloric acid is made in a furnace of firebrick, and the reaction involved is:



since this process is more economical and it is desired to obtain sodium sulfate, Na_2SO_4 .

closed by a well-fitting cork with two holes; through one of these passes a safety funnel *a*, and through the other the delivery tube *b*. These tubes must fit air-tight in the cork. It is well to cut the lower end of the delivery tube *b* diagonally (and also that of the tube *e*), or to file a small hole in the tube near its end, so that the drops which collect here shall not be carried along by the stream of gas.

The wash bottle *B* is a three-necked Wolff bottle, holding about 0.5 liter, and should be about twice as high as its diameter. The necks are closed with perforated corks through which pass the inlet tube *c*, the delivery tube *e*, and the safety tube *d*; the last prevents the liquid in *C*

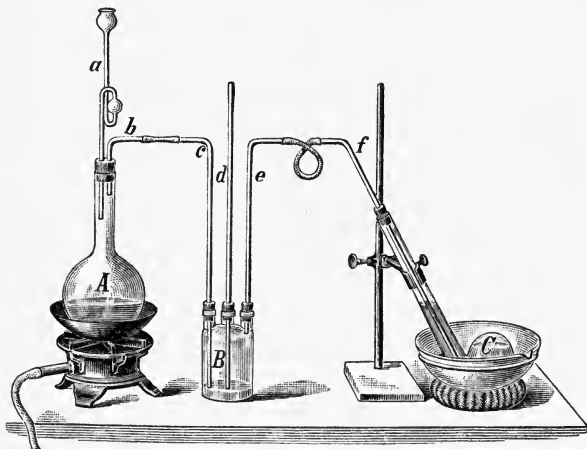


Fig. 1. Apparatus for the preparation of hydrochloric acid.

from being sucked back into *B*. (In the place of a Wolff bottle a flask can be used, fitted with a cork having three perforations.) The retort should hold about 400 to 450 cc, and the neck should be large enough to hold all the liquid which can be driven out by the air when the flask is placed diagonally. The tube *f*, which is slightly bent at its lower extremity, is supported by a cork, with a small groove cut lengthwise on its edge, in order not to close the retort completely.

The tubes *b* and *c* are connected by a short rubber tube, the tubes *e* and *f* by one somewhat longer.

Operation: After the apparatus has been tested and found air-tight, the flask, the wash bottle, and the retort are weighed.

The necessary quantity of distilled water is placed in the retort;¹ the wash bottle is filled one-fifth full of (commercial) concentrated hydrochloric acid, whose specific gravity has been determined by a hydrometer, and again weighed.² The amount of concentrated sulfuric acid to be used is calculated according to equation (3), account being taken of its specific gravity, and the acid is diluted with one-fifth its weight of water, (How? Use care!) that the evolution of gas may not be too violent. When the acid is cold it is poured through the safety funnel *a* into the flask, in which the requisite quantity of common salt has been already placed. The retort into which the gas is led is at first set in such position that the air expelled by pouring in the acid shall not collect in its body, but escape by the neck. By shaking the flask gently a uniform mixture of acid and salt is obtained, and then the flame under the sand bath is lighted.

As soon as white fumes are seen in the neck of the retort, and the clicking sound occasioned by the absorption of the hydrochloric acid is heard, the retort is turned so that the gas bubbles all come up into its body. A rapid evolution of hydrochloric acid now takes place, which may be increased by more heat under the flask; care must, however, be taken that the contents of the flask do not froth over. If the portion of the retort not under water is covered with a wet cloth, there is no danger of an appreciable loss of hydrochloric acid through incomplete absorption. Such a loss can be recognized by holding a glass rod wet with ammonia or a strip of blue litmus paper at the mouth of the retort. If the pressure in the retort increases during the operation so much, that the column of liquid in the safety tube *a* is insufficient to maintain an equilibrium, the pressure can be decreased by slightly turning the retort.

The end of the reaction is recognized by the following phe-

¹ Compare footnote to page 6.

² If water were placed in the wash bottle, so much hydrochloric acid would be absorbed that the product would not reach the required strength.

nomena: the frothing in the flask ceases; the tube leading to the wash bottle becomes hot (why?); the liquid in the retort sucks back through the tube *f*; air bubbles enter the wash bottle by the safety tube *d*. The flame under the sand bath is now turned down and the connection between *A* and *B* broken; the flame is raised again and the gas given off is tested. If no fumes of ammonium chlorid are formed about a glass rod moistened with ammonia, the operation may be considered at an end.

Time of Operation: About two hours.

Yield: To find the yield of hydrochloric acid, the weight and specific gravity of the contents of the retort and of the wash bottle must be determined. Calculation shows whether more or less hydrochloric acid is present in the wash bottle than at the beginning of the operation; an excess is to be added to the hydrochloric acid found in the retort, a minus quantity is to be deducted. If the operation has been carefully carried out, from 90 per cent. to 92 per cent. of the theoretical quantity should be obtained. Generally the product contains only 18 per cent. to 19 per cent. of hydrochloric acid.¹

Test: The product obtained will be free from arsenic if the sulfuric acid used was itself free. The product should be free from sulfuric acid and should leave no residue on evaporation.

By-product: *Hydrogen Sodium Sulfate, HNaSO₄.*

The contents of the flask solidify on cooling to a crystalline mass. To this is added its weight in water and all is brought to solution on a water bath. Filter and evaporate on the water bath in a porcelain dish until a crystalline scum begins to form

¹To ensure the preparation of 20 per cent. acid, not all the calculated amount (400 cc) of water should be placed in the retort, but a portion (say 50 cc) reserved. A stronger acid will then be obtained, which may be diluted to exactly 20 per cent.

on the surface. Then heat the dish with free flame over wire gauze, stirring constantly until all frothing has ceased. The temperature of the fused mass will now be about 250° . If the drop which adheres to the thermometer bulb be shaken on to a glass plate, it should solidify at once to a hard mass, upon which



Fig. 2. Apparatus for Casting in Sticks.

the thumb nail makes no impression. The contents of the dish are then either cast in an iron mould (Fig. 2) or poured out upon a smooth surface.

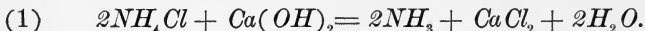
Yield : 95 per cent. of the theoretical amount.

2. Ammonia.

(By-product: *Granulated Calcium Chlorid.*)

Raw Materials : Ammonium chlorid (sal ammoniac), lime, concentrated ammonia.

Calcium hydroxid liberates ammonia from ammonium chlorid:



Calcium hydroxid is prepared from lime:



Exercise : *To prepare 500 grams of 10 per cent. aqueous solution of ammonia.*

Apparatus: The same as in Exercise 1.

Operation: Since lime contains not only magnesia, ferric oxid, etc., but also more or less water and carbonic acid (derived from the air), it is necessary in preparing the calcium hydroxid to use 20 per cent. more freshly burned lime than is required by equation (1). The lime is placed in a porcelain dish and over it is poured the quantity of water demanded by equation (2). The water which is lost through vaporization by the heat of slaking is to be replaced; this is easily accomplished if the dish was weighed while empty. After slaking, the lime should fall to a powder and feel dry to the touch. The time required depends upon the quality of the lime; in general two or three hours, including the time for the cooling of the lime, will be sufficient.

After examination has shown that the apparatus is air-tight, the required quantity of distilled water¹ is placed in the retort² and about 100 grams of ammonia (sp. gr. 0.945 to 0.960) is placed in the wash bottle. (The exact weight and specific gravity of the ammonia used must be determined!) Pour into the flask the quantity of slaked lime and ammonium chlorid required by equation (1) and wash down the neck and sides of the flask with a quantity of water sufficient to dissolve at 100° all the ammonium chlorid used. Close the flask quickly, mix the contents by shaking and warm upon the sand bath. The retort should be so placed that

¹ The experience obtained in carrying out Exercise 1 shows that in order to prepare a 10 per cent. ammonia solution it is best to reserve some 50 to 100 grams of the 450 grams of water required by theory. A somewhat stronger solution than 10 per cent. may then be expected and this can be diluted as demanded.

² Accuracy in carrying out this exercise is largely dependent upon the use of a retort of the proper size. There must be room for all the water used in the body of the retort when it is placed in its usual position.

the bubbles of air which enter it rise into its body. As soon as the ammonia begins to be absorbed, which is evident from the crackling noise, the retort should be freed from air by rotating it, and should then be firmly clamped in position. This reduces the pressure by lessening the height of the column of liquid in the neck of the retort. From time to time the increasing pressure in the retort may be regulated by a proper rotation. The retort is to be kept cool as in Exercise 1. If the vessel holding the retort contains three liters of water, this water will not rise in temperature more than five to ten degrees during the operation. The flame under the sand bath should be regulated so that the contents of the flask boil briskly. The contents of the wash bottle become more and more heated owing to the water which distils over,¹ and increase decidedly in volume.

The end of the operation is recognized by the tendency of the liquid in the retort to rise in the delivery tube. When this occurs, the heating is to be continued for half an hour, and then the gases which escape from the flask on breaking its connection with the wash bottle are to be tested. If no decided fumes of ammonium chlorid appear, when a glass rod moistened with hydrochloric acid is held in the escaping gas, the operation is over.

Time of Operation : About three hours.

Yield : The calculation of the product is carried out as in Exercise 1. By careful work it is possible to obtain 95 per cent. of the theoretical amount.

Test : The product should leave on evaporation no residue.

By-product : *Granulated Calcium Chlorid, CaCl_2 .*

While still warm the contents of the flask should be poured

¹ During the operation about 150 grams of water distill over into the wash bottle.

off from the lumps¹ generally present into a porcelain dish, and then boiled with constant stirring until the vapors given off cease to redden blue litmus paper. The contents of the dish are then diluted (with great caution!) with about 500 cc of water, poured into a beaker glass and allowed to settle over night. If the supernatant liquid is colored, the iron present is to be completely oxidized by adding a few grams of bleaching powder, stirred up with a little water, and afterward neutralizing the liquid with hydrochloric acid. If the liquid accidentally becomes acid, neutralize with lime water. After sedimentation, filter the colorless liquid through a corrugated filter [or on a Hirsch funnel by suction] and evaporate on a water bath in a porcelain dish until the liquid no longer decreases in volume.² Now heat over a wire gauze *with constant stirring* until the contents of the dish have become solid, and then, removing the wire gauze, continue the heating until a cold piece of glass held over the dish shows no more deposition of water.

The dehydrated calcium chlorid is very hygroscopic, and hence is used for drying gases, for the quantitative determination of water in elementary analysis, etc. It is advisable to break up the lumps at once and to fill the prepared tubes.

For this purpose empty the contents of the dish while hot into a porcelain mortar, break up the larger lumps into pieces the size of a pea, and screen off the powder, all these operations being carried out as rapidly as possible. It is best to use two sieves with different sized holes, so selected that pieces of the desired size will pass one sieve, but not the other. In the enlargement of the calcium chlorid tube a little plug of asbestos or glass wool is placed and then the calcium chlorid poured in;

¹ These lumps consist chiefly of calcium oxychlorid, $\text{Ca} \begin{smallmatrix} OH \\ Cl \end{smallmatrix}$

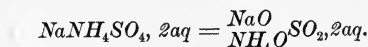
² If the liquid is allowed to cool at this stage, $\text{CaCl}_2 \cdot 6\text{aq}$ crystallizes out.

when nearly full another wad of asbestos or glass wool is added and the tube tightly stoppered.

If the calcium chlorid tube is to serve for quantitative work, it is necessary to lead a stream of dry carbon dioxid through it, in order that the calcium oxychlorid which is always formed in small quantities at high temperatures, may be changed into the neutral salt :



3. Sodium Ammonium Sulfate.



Raw Materials: Hydrogen sodium sulfate, ammonia.

The formation of this salt proceeds according to the equation:



Exercise: *To make sodium ammonium sulfate from the hydrogen sodium sulfate obtained as a by-product in Preparation 1, and ammonia of sp. gr. 0.88–0.90, using such quantities of ammonia and water that, after the mixture has cooled, 100 grams of double salt shall crystallize out without further evaporation.*

Operation : In a round-bottomed liter flask place whatever quantity of hydrogen sodium sulfate is at hand, with the necessary amount of water, calculated with due regard to the water present in the ammonia which is to be used. As soon as most of the salt has dissolved set aside about 10 cc of the solution, and then add with great care the requisite amount of ammonia to the contents of the flask. The solution will become heated (to about 80°C.) and will have an alkaline reaction. If it becomes cloudy,¹ filter into a porcelain dish. Then add with constant stirring enough of the solution which has been set aside

¹ In consequence of the separation of ferric hydroxid, alumina, magnesia or other impurities contained in the salt or the sulfuric acid used in making the hydrogen sodium sulfate.

to render the whole neutral in reaction. Set in a cool place for crystallization.

Sodium ammonium sulfate is apt to form *supersaturated* solutions, hence it often happens that even after standing several days no salt crystallizes out. In such a case evaporate a few drops of the solution upon a watch glass until crystals appear, and sow these in the supersaturated solution.

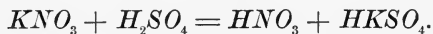
Properties: Rhombic crystals; one part of $\text{NaNH}_4\text{SO}_4, 2\text{aq.}$ dissolves in 2 1-7 parts of water at 15° .

4. Nitric Acid.

(**By-product:** *Hydrogen potassium sulfate, HKSO_4 .*)

Raw Materials: Saltpeter and concentrated sulfuric acid.

The preparation takes place according to the following equation:



Exercise: *To prepare 100 grams HNO_3 .*

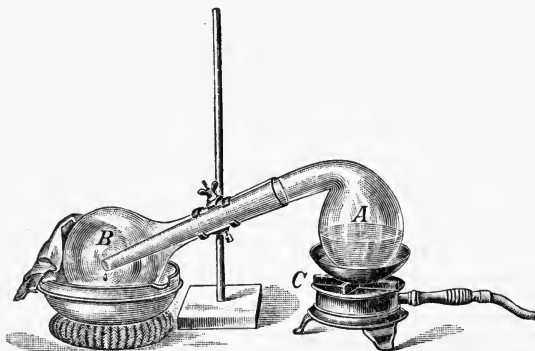


Fig. 3. Preparation of Nitric Acid.

The Apparatus consists of a retort *A* and a round-bottomed flask *B*, which are fitted to each other as shown in Fig. 3. The retort rests on a sand bath over a Fletcher burner, *C*. The flask is placed in a dish of

water to keep it cool, and is supported by a stand to which the neck is clamped.

The body of the retort should hold about 0.7 to 0.8 liter and the flask about a liter. The retort projects into the flask so far that when the neck of the flask closes tightly around the neck of the retort, the lower end of the latter reaches the middle of the flask.

If the dish in which the flask rests holds about 3 liters of water for cooling, it will not be necessary to renew the water during the operation.

Operation: Place the saltpeter in the dry retort and add the required amount of concentrated sulfuric acid through a funnel whose lower end reaches the body of the retort. Be careful in withdrawing the funnel not to touch the sides, and also that no saltpeter adheres to the neck. On agitating the retort the contents become warm.

Fit retort and flask together, place under a hood, fill the porcelain dish with water and heat the sand bath with a small flame. At the beginning of the operation yellowish brown fumes appear, owing to the reduction of the nitric acid by the dust present in the saltpeter; at the end of the reaction similar fumes are given off from the decomposition of nitric acid by heat. The flame should be so regulated that the fumes shall condense completely in the neck of the retort and in the flask; this can be assisted by covering the flask with a wet cloth. When the contents of the retort, at first partly at least liquified, have become solid again, the heat should be increased. The end of the operation is recognized by the fact that drops fall into the flask only occasionally, and the fumes in the retort become darker. The sand bath should now be carefully removed, a wire gauze substituted and the heat continued until the contents of the retort are melted. The retort is now removed from the neck of the flask, the hand being protected by a towel or asbestos holder. The fused hydrogen potassium sulfate is poured out into a thin 400 cc porcelain dish which stands on a hot sand bath. In order to free the product from the last trace of saltpeter, heat in the porcelain dish for a short

time to about 280° over a wire gauze and then pour into an iron mold or on a flat surface.

Time of Operation: 2 to $2\frac{1}{2}$ hours.

Yield: About 100 grams nitric acid, containing 95 to 97 per cent. HNO_3 .

The strength of the nitric acid is best determined by titration.

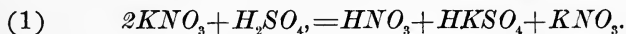
Properties and Tests: A slightly yellowish liquid, fuming in the air and beginning to boil at 86° . It becomes heated on mixing with water (use care!) The product should be free from sulfuric acid. If the saltpeter and the sulfuric acid are free from chlorin the nitric acid will be also.

5. Red Fuming Nitric Acid.

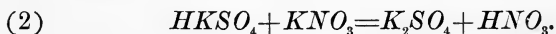
(By-product: *Potassium Sulfate, K_2SO_4 .*)

Raw Materials: Saltpeter, concentrated sulfuric acid.

Red fuming nitric acid is a solution of NO_2 in nitric acid, with a little water ($HNO_3 + NO_2 + \frac{1}{2}H_2O$.) It is prepared by the action of *one* molecule of concentrated sulfuric acid on *two* molecules of saltpeter. At first by the moderate heating of the mixture nitric acid is formed, together with hydrogen potassium sulfate, even though there is an excess of saltpeter present:



At higher temperature the hydrogen potassium sulfate reacts with the unchanged saltpeter. The nitric acid which is formed is unstable at this temperature and decomposes (at 256°) into NO_2 , O , and H_2O :



The NO_2 dissolves in the nitric acid which was produced in the first stage of the operation.

Exercise: *To prepare 100 grams of red fuming nitric acid.*

Apparatus: The same as in Preparation 4.

Operation : At first as in Preparation 4. When the contents of the retort have become completely liquid, and the nitric acid has ceased to drop in the flask, the first stage of the decomposition is nearly completed. The sand bath is now replaced by a wire gauze, and the heating continued carefully. Soon the contents of the retort begin to froth, but this soon ceases, and by careful regulation of the flame, it is possible to avoid any frothing over of the contents. The fumes which fill the entire apparatus become darker and at last blackish brown. If the contents of the retort solidify, the heat must be increased, but not so much that any large quantity of brown fumes escapes between the necks of flask and retort.

Time of Operation : About three hours.

After the apparatus is quite cold, pour the distillate into a glass-stoppered and weighed bottle.

The amount of red fuming acid obtained should be 90 to 95 grams.

Test : The product should be free from sulfuric acid.

By-product : *Crystallized Potassium Sulfate, K_2SO_4 .*

The potassium sulfate remaining in the retort is dissolved in the amount of water required for its solution at 100° , and the boiling, clear solution poured into a wide porcelain dish. On cooling, 60 to 70 grams of potassium sulfate should crystallize out ; by evaporating the mother liquor an additional 40 to 50 grams of crystals is easily obtained.

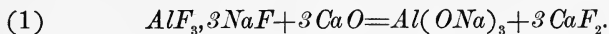
Properties : Rhombic crystals, anhydrous. Soluble in 10 parts of water at 15° ; 4 parts at 100° ; melting point 1078° (Victor Meyer.)

6. Soda and Alumina from Cryolite.

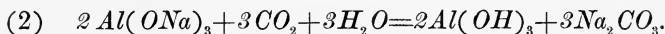
(**By-product:** *Calcium Fluorid.*)

Raw Material : Finely powdered cryolite, calcined marble, carbon dioxid.

Calcium hydroxid decomposes cryolite at the boiling point of water, calcium fluorid and sodium aluminate being formed:



If carbon dioxid is led into a solution of sodium aluminate, aluminum hydroxid and sodium carbonate are formed:



Exercise : *Convert 100 grams of cryolite into alumina and soda.*

Operation : Burnt marble¹ (about 5 per cent. more than is called for by equation (1)) is slaked with the requisite amount of water in a porcelain dish holding about a liter, and then stirred with 500 grams of water, forming milk of lime. The cryolite, ground to the finest possible powder, is added to the milk of lime, and the mixture heated over a wire gauze with constant stirring to boiling. The boiling is continued for about an hour, water being added from time to time to replace that lost by evaporation. The contents of the dish thicken more or less, but by constant stirring spattering can be avoided.

The progress of the decomposition may be best followed by a microscope. When the reaction is complete, the regular, sharp-edged fragments of cryolite are no longer recognizable. The mixture is then diluted with about 500 cc of hot water and immediately filtered. For this purpose a linen cloth is used,

¹ The lime should be as free as possible from iron, and hence burnt marble is the best form to use.

stretched across a wooden filter frame¹ which rests upon a porcelain dish (see Fig. 4.)

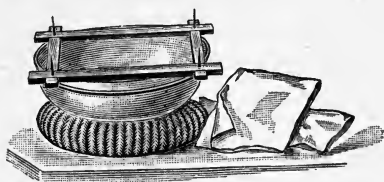


Fig. 4. Tenaculum and Strainer.

The residue left on the linen cloth is washed repeatedly with warm water, each time being well stirred up. In this way the residue can be washed to faint alkaline reaction by the use of from $1\frac{1}{2}$ to 2 liters of water. When the washing is ended the cloth is removed from the frame and wrung out with the hands.

The residue consists chiefly of calcium fluorid, with the excess of added lime (and calcium carbonate) and is dried and preserved for Preparation 16.

The cloudy percolate is passed through a paper filter. Into the clear solution carbon dioxid is led by a wide glass tube until the alumina is completely precipitated.

The alumina, like the calcium fluorid, is best filtered on linen cloth, washed and then dried. The clear filtrate² is evaporated to about 200 grams, when on standing 120 to 150 grams of sodium carbonate should crystallize out.

The amount of alumina obtained should approach 95 per cent. of the theoretical.

¹ This form of filter support (known as a tenaculum), which has been in use for centuries, is a square frame of wood. The points of the nails which hold the corners together project far enough out of the wood for the linen to be hooked on to them. The portions beyond the corners serve to support the frame on the rim of a porcelain dish. The liquid which is in this manner separated from the solid material is known as the percolate; the apparatus is called a percolator, and the operation percolation. The percolate is generally cloudy and must be clarified by filtration through filter paper.

² If this filtrate has come in contact with the wood of the tenaculum it may have a yellowish tint; it can readily be decolorized by boiling with animal charcoal.

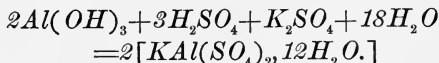
Properties and Tests of the Soda: (Na_2CO_3 , 10aq.) Monoclinic crystals, which effloresce in the air, melt at 34° , and by continued heat lose all their water of crystallization (dried or calcined soda.) The product should be free from lime and alumina. This method of preparation avoids the usual impurities of the Leblanc and ammonia processes (chlorin, sulfuric acid and ammonia.)

7. Alum.

$\text{KAl}(\text{SO}_4)_2$, 12aq.

(Intermediate Product: *Aluminum Sulfate.*)

Raw Materials: Alumina, potassium sulfate,¹ concentrated sulfuric acid. The equation for the preparation of alum is as follows:



Exercise: To convert the aluminum hydroxid,² obtained in Preparation 6, into alum. The amount of water to be used is such that, on cooling, one-half the product (alum) should crystallize out.

Operation: Dilute the amount of concentrated sulfuric acid required to convert the alumina into aluminum sulfate with twice its weight of water. Dissolve the alumina with heat, and filter the hot solution through a hot water funnel [the use of suction is advantageous.] On cooling, the solution solidifies to a crystalline mass, consisting of pearly flakes of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, 18 aq.

¹ Obtained as a by-product in Preparation 5.

² This preparation does not have in general the formula $\text{Al}(\text{OH})_3$, but a quantity of water is present varying with the method of drying. This may be expressed by the formula $\text{Al}_2\text{O}_3 + x\text{H}_2\text{O}$. Determine in a weighed sample of this aluminum hydroxid the amount of alumina, by heating to redness in a platinum crucible.

After the aluminum sulfate has been again brought into solution by heat, it is mixed with the solution of potassium sulfate, which contains the balance of the water calculated as necessary.

Properties : Colorless, transparent octaedra, generally presenting also cube faces; soluble in 8 parts of water at 15°.

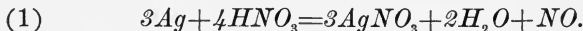
8. Silver Nitrate from Coin Silver.

(Intermediate Product: *Pure silver.* By-product: *Copper.*)

Raw Materials : Coin silver, nitric acid, hydrochloric acid, soda, etc.

Exercise: *Separate a 25-cent piece into silver, copper (and gold), and convert the silver into silver nitrate.*

Operation : Cover the coin with nitric acid free from chlorin, of specific gravity not above 1.2, using for the purpose only a small excess of the acid beyond that required by the formula:



A few little black flakes of gold remain undissolved. Collect these on a small filter, and precipitate the blue solution with hydrochloric acid. After filtration, wash the silver chlorid until the wash-water ceases to show any reaction for copper. After drying, mix the silver chlorid thoroughly with

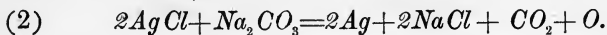


Fig. 5. Reduction of Silver Chlorid.

double its weight of calcined soda, put the mixture in a hollow on a piece of charcoal *A* (Fig. 5), and heat before the blast lamp¹. In order to prevent the dissipation of the heat, it is

¹ [The silver chlorid may be reduced more rapidly in a small Hessian crucible in a furnace.]

advantageous to place a second piece, *B*, of obliquely cut charcoal over *A*, as shown in Fig. 5.

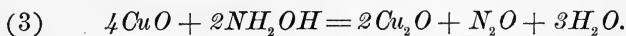


The globules of reduced silver flow together; the sodium chlorid formed and the excess of soda are absorbed by the charcoal. The fused silver absorbs oxygen, which is given off again at the instant of solidification ("spitting" of silver). The upper surface of the regulus therefore appears rough.

Yield : From 5 grams of coin a globule of silver weighing 4.44 grams can be easily obtained (in place of the theoretical quantity 4.5 grams).

For the Preparation of Silver Nitrate the pure silver is redissolved in nitric acid. The solution is evaporated to dryness in a porcelain dish on the water bath; the residue is then placed in a small porcelain crucible and the last trace of moisture driven off under a hood. The silver nitrate is fused by careful heating over a Bunsen burner and immediately poured out upon a porcelain plate.

To Obtain the Copper, the filtrate from the silver chlorid precipitate is evaporated to dryness on the water bath, the residue dissolved in a small quantity of water, and the copper precipitated as cuprous oxid, by sodium hydroxid and hydroxylamin hydrochlorid (or other suitable reducing agent.)



The cuprous oxid is filtered, thoroughly washed and dried. It is placed in a bulbed reduction tube of hard glass, connected with a hydrogen generator (see Fig. 6) and, after the air in the tube has been completely displaced and the escaping hydrogen lighted (using necessary precaution), is heated with a low flame. [A combustion furnace with a wide glass tube may be used, the cuprous oxid being placed in a porcelain boat.]

To Recognize the Gold: Burn the filter paper which contains the black residue left from the solution of the coin in nitric acid. Cover the ashes with a few drops of aqua regia and

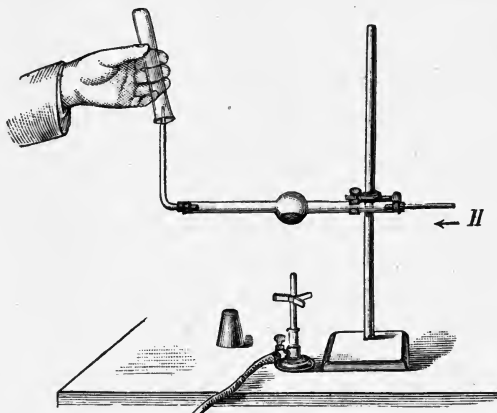


Fig. 6. Reduction of Cuprous Oxid.

evaporate the solution to dryness on a water bath. Dissolve the residue in a few drops of dilute hydrochloric acid, filter, and add to the filtrate a trace of stannous chlorid or ferrous sulfate solution.

9. Liquid Sulfur Dioxid.

(By-products: *Ferrous sulfate, copper sulfate.*)

Raw Materials: Concentrated sulfuric acid, copper sulfate, iron filings free from grease,¹ rock salt, carbon bisulfid.

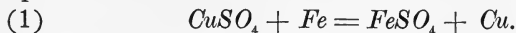
¹ To free iron filings from grease they are placed after drying in a flask, covered with carbon bisulfid and shaken thoroughly, first stoppering the flask. After the filings have settled the carbon bisulfid is poured off and the process repeated once or twice. The filings are then washed on a filter with carbon bisulfid and allowed to dry. The carbon bisulfid is recovered from the united solutions by distilling on a water bath. (Compare with Fig. 15.) Use care in working with carbon bisulfid! (Why?)

Exercise: Prepare 100 grams of sulfur dioxid by the action of concentrated sulfuric acid upon copper, which has been precipitated from a solution of copper sulfate by the action of metallic iron. Condense the gas to a liquid by cold.

A. Precipitation of Copper from Copper Sulfate.

(By-product: *Ferrous sulfate.*)

The precipitation of copper takes place according to the equation:



Operation: The quantity of copper needed for the exercise is calculated from equation (2) (page 24). The corresponding quantity of crystallized copper sulfate ($\text{CuSO}_4, 5\text{aq}$) is dissolved in a porcelain dish holding about $1\frac{1}{2}$ liters, using sufficient water (previously boiled) to dissolve the copper sulfate at 80° . The amount of iron filings should be 10 per cent. more than that required by theory, because the iron is generally not free from oxid and may contain other impurities. After the copper sulfate is completely dissolved and the solution is heated to 70° or 80° , carefully add the iron, a little at a time, while stirring. The contents of the dish become heated to boiling by the reaction. When the reaction has subsided, if the solution is still colored blue, stir with a wide strip of bright sheet iron until the blade of a pocket knife dipped in the solution ceases to receive a coating of copper. Filter the hot solution through a hot water funnel¹ into a porcelain dish, leaving the copper as far as possible on the bottom of the dish, and decant with about 100 cc of boiling water. When no more liquid drops from the funnel, remove the filter paper and spirt the copper on it back into the dish containing the mass of the copper, by means of a wash bottle, and clean the strip of sheet iron in the same way.

¹ [A Hirsch funnel with suction is advantageous.]

Time of Operation : 1 to $1\frac{1}{2}$ hours.

In order to free the copper from the iron mingled with it, treat it with dilute sulfuric acid on a water bath. For filtering and washing the copper, a sand filter is advantageously used. This is prepared by placing a bulbed tube¹ in a funnel and covering it with a layer of sea-sand about two centimeters deep. (Fig. 7.) As long as the liquid runs through distinctly colored green, it is to be collected separately, and the washing then continued until the wash-water no longer has an acid reaction. Spread the copper on a filter paper and dry it in the air. When dry the copper appears as a red-brown powder, which receives a metallic lustre by rubbing in an agate mortar. The amount of copper obtained should correspond closely to theory.

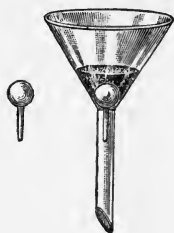


Fig. 7. Sand Filter.

By-Product : *Ferrous Sulfate, $\text{FeSO}_4, 5\text{aq.}$*

From the solution which has been filtered from the copper, there should crystallize about 200 grams of ferrous sulfate. Pour off the mother liquor and drain the crystals on a Hirsch funnel. The mother liquor and the wash-waters, as far as they are colored distinctly green, are united and evaporated on a water bath. In this way some 200 grams more of ferrous sulfate may be recovered.

Yield : 90 to 95 per cent. of theoretical.

B. Preparation and Condensation of the Sulfur Dioxid.

(By-product: *Copper Sulfate.*)¹

The principal reaction between copper and hot concentrated sulfuric acid is:

¹ A bulb is blown on the end of a small glass tube and the other end is fused off.



The boiling point of sulfur dioxid at ordinary pressure is -8° . When cooled below this temperature it is condensed to a colorless liquid. By means of a freezing mixture of snow or ice and salt, a temperature of -21° is easily attained.

When gases are to be condensed they should be pure and dry. Acid gases are usually dried over concentrated sulfuric acid, unless they have a reducing action upon it. It may happen that in the rapid evolution of sulfur dioxid some of the sulfuric acid may be carried along with it mechanically; to absorb such sulfuric acid, the stream of gas is passed over solid potassium sulfate:



Apparatus: See Fig. 8. The flask *A* and the wash bottle *B* are arranged as in Preparation 1 (Fig. 1). From the wash bottle the gases pass through the tube *g*, which is filled with crystals of potassium sulfate.

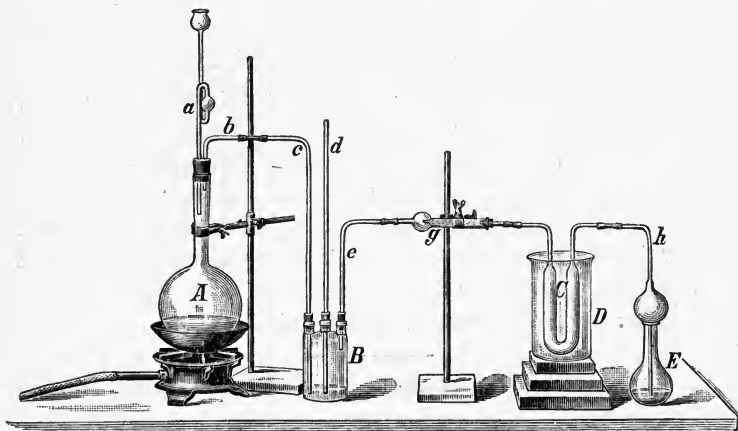


Fig. 8. Preparation of Liquid Sulfur Dioxid.

The gases then enter the U-shaped tube *C*, in which the liquid sulfur dioxid is condensed. The U-tube stands in an earthen vessel *D*, filled with the freezing mixture, and is connected with the bulbed tube *h*, which

dips just below the surface of water in flask *E*. This water serves to absorb any sulfur dioxide which is not condensed in the U-tube.

The tube *g* is of the general form and size of a calcium chloride tube, and may be filled with the potassium sulfate obtained as a by-product in Preparation 5; the salt should be first freed from powder by sifting.

The branches of the U-tube *C* are about 25 cm long and 15 to 18 mm in diameter; both ends are drawn out and bent at right angles.

The bulbous tube *h* rests by its bulb on the neck of the flask *E*. The length of the tube below the bulb is such that when 100 to 150 cc of water are in the flask, the end dips just below the surface of the water.



Fig. 9.

Fig. 9 shows the tube prepared for sealing up the sulfur dioxide, standing in a glass cylinder filled with freezing mixture. The tube is made from thick walled tubing, and is about 40 cm long. One end is sealed off and the other drawn out into a thick walled capillary tube.

Operation : After the apparatus has been tested in all its parts and found to be air-tight, the copper is placed in the flask; sufficient concentrated sulfuric acid is placed in the wash bottle for the entrance tube to dip about 2 cm below the surface; the earthen vessel around the U-tube is filled with alternate layers of snow or pounded ice (3 parts) and rock salt¹ (1 part). 700 grams of concentrated sulfuric acid² are then poured upon the copper. The flask is shaken and the lamp lighted under the sand bath. As soon as the evolution of bubbles in the flask shows that the copper has begun to act upon the sulfuric acid, the flame is extinguished. The heat of reaction is generally sufficient to keep up a rapid evolution of gas. The air expelled by the stream of gas escapes by the bulbous tube. The sulfur

¹ The quantity depends upon the size of the vessel; for a 1 liter vessel 700 g ice and 230 g salt are sufficient. If the vessel holds 3 or 4 liters once filling with the freezing mixture will suffice for the whole operation.

² This is more than double the theoretical quantity; why is an excess of sulfuric acid necessary?

dioxid carried along by this air is absorbed by the water in the flask. After a short time this escape of air bubbles ceases.

The flame under the sand bath should not be again lighted until the rapidity with which the gas bubbles through the wash bottle begins to lessen. It should then be so regulated that there should be a fairly rapid evolution of gas, but not too much frothing of the contents of the flask. As the liquified sulfur dioxid collects in the U-tube the pressure in the apparatus rises. It is well to have about 20 grams of mercury at hand, to pour into the safety funnel, when the height of the column of liquid in it is no longer sufficient to overcome the increased pressure.

Toward the end of the operation the upper part of the flask becomes covered with a yellowish film of sulfur,¹ which gradually increases. Some sulfur may also be carried over into the wash bottle, though generally without any danger of stopping up the tubes. When the connection tubes and the contents of the wash bottle have become hot, the operation is completed.

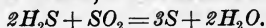
Time of Operation: $2\frac{1}{2}$ to 3 hours.

The tube prepared for the sulfur dioxid is weighed and then surrounded in a high glass cylinder with a freezing mixture. The liquid in the U-tube is poured in with great care (under a draught) and the tube closed by fusing before a blast lamp or a blow pipe the part which has been drawn out.

The yield is usually not more than 50 per cent. of the theoretical; it is influenced by the incomplete condensation of the first portion of the gas coming over with the air, by secondary reactions, and lastly by decided loss in filling the tube.

Properties: Colorless liquid, boiling at -8° (Pierre) and

¹ Hydrogen sulfid is formed, which reacts with the sulfur dioxid:



solidifying at -76° (Faraday.) Its tension in closed vessels is at 0° , 1.7 atmospheres; at 10° , 2.3 atm.; at 20° , 3.3 atm., etc.

By-product: *Copper sulfate, $CuSO_4, 5aq.$*

Add with care about 750 cc¹ of water to the contents of the flask.

Boil the mixture and filter the blue solution from the insoluble black substance into a porcelain dish. On cooling, the greater part (about 300 grams) of the copper sulfate crystallizes out. Wash the residue remaining on the filter paper with hot water until the wash water has no longer an acid reaction. As long as the filtrate is distinctly blue, collect it separately. Add the blue filtrates to the mother liquor from the crystals, and evaporate on the water bath to crystallization. An additional 50 to 60 grams of crystals may be obtained in this way.

Yield: Nearly 90 per cent. of the copper sulfate originally used. About 10 grams or less of black substance is left upon the filter paper. Determine its composition by qualitative examination and account for its formation.

Properties: Blue, triclinic crystals.

The product should not contain iron.

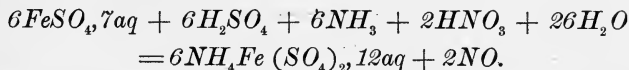
10. Iron Ammonium Alum.



Raw Materials: Ferrous sulfate, ammonia, concentrated sulfuric acid, nitric acid.

¹ This is much more water than corresponds to the solubility of the blue vitriol in the water; its solubility is decidedly lessened by the presence of the excess of sulfuric acid.

The preparation of iron ammonium alum is according to the equation:



Exercise : *Prepare 500 grams of iron ammonium alum in such a manner that at the end of the reaction two-thirds of the product shall crystallize out, on cooling, without further evaporation of the solution.*

Operation: The ferrous sulfate to be used is that which was obtained as a by-product in Preparation 9; the nitric acid should have sp. gr. 1.30 to 1.40; the ammonia sp. gr. 0.90 to 0.95; the sulfuric acid should be concentrated. Calculate the required quantity of each ingredient, paying particular attention to the water present in each; from the solubility of the alum is calculated the further amount of water which must be used. Add to the ferrous sulfate in a 2-liter flask the calculated amount of water and then (with great care!) the concentrated sulfuric acid. Place the flask over a water bath under a good draught, hang in the mouth of the flask a funnel and add the nitric acid in small portions. Immediately upon the addition of the first drops the liquid becomes dark brown and soon the flask is filled with brown-red fumes. Upon the addition of the last portions of the nitric acid a violent evolution of gas may take place; hence, much care must be used. Heat the contents of the flask over a wire gauze, remove the funnel from the neck of the flask and boil until the colored fumes cease to be evolved. Withdraw a few drops of the liquid with a pipette and after dilution test for ferrous iron. If the oxidation is complete, pour the contents of the flask into a porcelain dish and add the ammonia with constant stirring. In this operation no permanent precipitate should be formed. The clear liquid should have a greenish brown color.

Time of Operation: 1 to $1\frac{1}{2}$ hours.

Yield: On cooling the liquid, from 200 to 250 grams of iron ammonium alum should be obtained, generally in beautiful crystals. By concentration of the mother liquor the yield may readily be increased by some 100 grams.

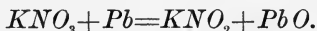
Properties: Pale violet, transparent octaedra, soluble in 3 parts of water at 15° .

II. Potassium Nitrite.

(By-product: *Lead Oxid.*)

Raw Materials : Saltpetre, lead.

In fused condition at high temperature saltpetre and lead react upon each other according to the following equation :



This reaction goes on spontaneously at a temperature which is somewhat above the melting point of lead (334°) and saltpeter (340°). It is impossible, without special forms of apparatus, to regulate temperatures of this intensity within narrow limits, and this is especially true when the temperature is modified by the heat of reaction. When saltpeter is heated by itself to a temperature considerably above its melting point it is decomposed partially into oxygen and potassium nitrite, while at a still higher temperature the nitrite is in turn decomposed into oxygen, nitrogen and potassium oxid. In the preparation of potassium nitrite these secondary reactions cannot be wholly avoided. Furthermore, a part of the saltpeter can easily fail to come into contact with the lead. For this reason it is best to use somewhat less lead than is demanded by the equation.

Exercise: Convert 250 grams of saltpeter into potassium nitrite as above described.¹

¹ For 250 grams saltpeter 400 grams lead are sufficient.

Apparatus : To reach the temperature demanded for the operation, a large gas furnace (after Rössler, Müncke, Perrot, etc.) or an arrangement for charcoal heating is required.¹ The heating of the saltpeter and lead is best carried out in a flat round iron pan, about 30 cm in diameter with a long handle. For stirring, a long iron spatula with a wooden [or asbestos] handle is necessary.

Operation : After the saltpeter has been melted in the iron pan over a gas flame or charcoal fire, add 50 to 60 grams of lead and stir together with the iron spatula till all the lead is oxidized. The heat must be so regulated that only a very slight evolution of gas takes place; it is impossible to avoid all decomposition. The remainder of the lead is to be added to the melted mass in portions of about 50 grams, each portion

being stirred thoroughly before the next is added. After each stirring no large globules of fused lead should be visible. As the quantity of lead oxid increases the melt thickens. Toward the end of the operation the heat is increased very carefully, but the bottom of the pan must not become more than faintly red hot. In the pasty mass spots of incandescence are often visible. When all the lead (400 grams) has been added and fully oxidized, take the pan from the fire, continuing the stirring



Fig. 10. Portable Furnace for Charcoal Firing.

until the melt solidifies to a lumpy mass which may be readily removed from the pan.

Time of Operation : About 1 hour.

After the melt is cold, it is placed in a strong stand glass

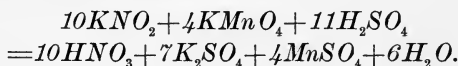
¹ For this purpose a portable furnace of strong sheet iron lined with firebrick is sufficient. The dimensions may be 0.4 meter high and 0.3 meter square, as is shown in Fig. 10.

and covered with about 250 grams of water, which has already been used to clean the pan. When the lumps have become disintegrated, pour the solution from the heavy sediment into a beaker glass, and stir 100 cc of warm water into the sediment and decant. Repeat this ten or twelve times, each time using about 100 cc of hot water. Then pour the litharge stirred up with water on to a filter, leaving the unchanged lead in the glass. Wash the litharge on the filter.

The united extracts give about 1.5 liters of solution and have an alkaline reaction. After neutralization with dilute sulfuric acid added drop by drop, filter, and evaporate the clear solution on the water bath till its weight is about 300 grams. On cooling, the greater part of the undecomposed saltpeter (50 to 75 grams) crystallizes out, while the potassium nitrite remains in solution. The solution, separated from the crystals, is now evaporated, with constant stirring,¹ to dryness on a sand bath in a thin walled porcelain dish. It is then fused over a free flame and poured in a mould or on a porcelain plate. The product should be placed in a tightly stoppered bottle just as soon as it is sufficiently cool to handle.

Yield : 1. Potassium nitrite: 95 to 97 per cent. of the theoretical amount from the saltpeter used (the amount taken, less that recovered); 2. Lead oxid: nearly the theoretical amount.

Test of the Potassium Nitrite : The product always contains some saltpeter,² but should be free from lead. The determination of the percentage of potassium nitrite in the product is carried out by titrating with potassium permanganate in a sufficiently dilute solution:



¹ Great care must be taken to shield the eyes from the spattering of the hot mass.

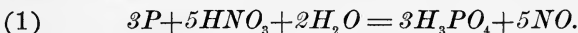
² Nitric acid is to be tested for after the nitrous acid has been decomposed by urea (see page 51.)

12. Phosphoric Acid.

(Orthophosphoric acid, H_3PO_4 .)

Raw Materials : Red ('amorphous') phosphorus, nitric acid, sp. gr. 1.21 to 1.24; (alcohol and ether.)

Both yellow and red phosphorus are oxidized by the action of nitric acid to phosphoric acid. If the nitric acid is stronger than that which corresponds to sp. gr. 1.24 the reaction goes on spontaneously with great violence. Yellow phosphorus is apt by this action to be spattered out of the liquid and ignited. If the nitric acid is weaker, the oxidation proceeds very slowly. The red phosphorus is much more quickly and safely converted into phosphoric acid, since by not melting it offers a much larger surface to the action of the acid, and it does not ignite at the boiling point of the nitric acid. The reaction takes place approximately according to the following equation:



Exercise : Convert 31 grams of red phosphorus into phosphoric acid.

The red phosphorus is first to be washed¹ with water. For this purpose stir about 60 grams of red phosphorus² with water in a beaker glass. After the phosphorus has settled, decant through a filter, and repeat this until the wash water has but a very weakly acid reaction; then wash the phosphorus on to the filter. After very thorough washing with water, rinse off with alcohol and then with ether, in order to be able to dry the phosphorus more quickly. Spread the filter with the phosphorus on absorbent paper to dry.

Operation : Place the quantity³ of nitric acid (sp. gr. 1.21

¹ Commercial red phosphorus contains as impurities phosphoric acid, phosphorous acid, arsenic, tin, iron, etc.

² 60 grams in order to have sufficient purified phosphorus for Preparation 23.

³ Actually, less than the theoretical amount of nitric acid is used, since in the reaction some N is formed as well as NO , and nitric acid is partly regenerated (in what way?)

to 1.24) required by equation (1) in a round-bottomed $\frac{2}{2}$ liter flask, add at first 10 grams phosphorus and set the flask on a straw ring under a hood.

If no marked heating takes place spontaneously within ten minutes, warm the flask upon a water bath which has been already prepared and heated, but continue the warming only till an evolution of gas begins and colored gas is visible in the flask. Then take the flask immediately from the water bath, place it again upon the straw ring, and hang a large funnel in the neck. The reaction becomes very quickly more active and the liquid begins to froth and boil; brown fumes escape from the flask, a part of which condense on the funnel and fall back into the flask. When the evolution of gas has ceased and the reddish brown color of the fumes in the flask has changed over into yellowish-brown, remove the funnel and add 5 grams more of phosphorus. The reaction begins anew and goes on as before. The remainder of the phosphorus is added in portions of about 5 grams, the reaction being allowed to subside each time before more phosphorus is added.

Time of Operation: $1\frac{1}{2}$ to 2 hours.

The contents of the flask consist of phosphoric acid, phosphorous acid, the excess of nitric acid, and are generally colored by the brownish-black arsenic which has remained undissolved. This liquid after cooling is poured into a retort holding about $\frac{3}{4}$ liter, and most of the excess of nitric acid is distilled off on a sand bath (see Fig. 3.) Toward the end of the distillation a rather violent reaction again takes place, which is caused by the oxidation of the phosphorous acid. When this occurs, dark brown fumes are given off and in part escape from the neck of the receiver. The reaction ceases suddenly and the distillation is then stopped.¹

¹ The distillate consists of about 150 to 180 grams of 10 to 12 per cent. HNO_3 .

The residue in the retort is poured into a flask and diluted with water to about a liter. Hydrogen sulfid is then led into the warm liquid for two or three hours, to precipitate the arsenic, which has been dissolved, and the whole is allowed to settle over night. The next morning if the contents of the flask smell strongly of hydrogen sulfid, the yellow, flaky precipitate¹ is filtered off; otherwise hydrogen sulfid is again led in until all the arsenic is precipitated.

The clear filtrate is now evaporated on a water bath in a porcelain dish until its volume ceases to diminish. It is then transferred to a smaller, thin-walled dish, and heated first on a sand bath and then over wire gauze until a thermometer in the liquid stands at 180°. Before heating on the sand bath remove a small sample from the dish and test for phosphorous acid. If silver nitrate is reduced by boiling with the diluted sample, add 10 to 20 grams of nitric acid of sp. gr. 1.21 to the contents of the porcelain dish. The finished product is to be immediately placed in a previously warmed, glass-stoppered bottle.

Yield: 90 to 95 grams of phosphoric acid, in place of ? grams.

Properties and Tests: Colorless, syrupy mass, which solidifies suddenly with evolution of heat on adding a crystal of phosphoric acid. Heated above 180° it is gradually changed with loss of water into pyrophosphoric acid. Slight heat only is developed on mixing the acid with water. In aqueous solution magnesia mixture gives a white, crystalline precipitate; ammonium molybdate gives a yellow precipitate, insoluble in nitric acid, but soluble in ammonia; silver nitrate with a little ammonia gives a lemon-yellow precipitate (distinction from pyrophosphoric acid); it does not coagulate albumen (distinction from metaphosphoric acid.) The product should be free from phosphorous acid and from arsenic compounds.

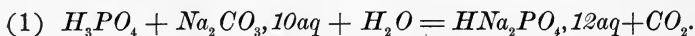
¹ A qualitative examination of the precipitate, which often amounts to more than a gram, will show whether it consists of As_2S_3 only, or also contains SnS_2 .

13. A. Disodium phosphate, B. Sodium ammonium phosphate, C. Pyrophosphoric acid, D. Metaphosphoric acid.

Raw Materials: Orthophosphoric acid, crystallized soda, ammonium chlorid, sugar of lead, hydrogen sulfid. (Alcohol.)

A. Disodium Phosphate.

Exercise: Convert 75 grams of the phosphoric acid obtained in Preparation 12 into crystallized disodium phosphate according to the equation:



The quantities to be used are such that on cooling the solution after reaction, two-thirds of the product shall crystallize out.

Operation: Dilute the phosphoric acid with the required amount of water, account being taken of the water of crystallization in the soda. Warm the solution and slowly add the calculated quantity of soda crystals. The solution should be only slightly alkaline¹ in reaction. Let the solution stand over night and then drain the crystals on a Hirsch filter. After the mother liquor has drained away as far as possible, dry the crystals by pressure between filter paper.

Yield: About 130 grams of disodium phosphate.

Properties: Monoclinic prisms, which effloresce rapidly in the air; the aqueous solution has an alkaline reaction. On heating, sodium pyrophosphate is formed.²

¹ I. e., a sample of it should become acid on the addition of very few drops of hydrochloric acid.

² For solubilities see pages 72, 73.

B. Sodium Ammonium Phosphate.

Exercise: Convert 150 grams of disodium phosphate into sodium ammonium phosphate according to the equation:



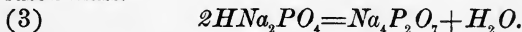
Operation: Dissolve the disodium phosphate and also the equivalent amount of ammonium chlorid in the smallest possible quantity of hot water and mix the solutions. The product which crystallizes out contains sodium chlorid and must be purified by recrystallization.

Properties: Sodium ammonium phosphate, also called 'phosphorsalt', 'salt of phosphorus,' and 'microcosmic salt,' crystallizes in monoclinic prisms, which effloresce gradually in the air and lose their ammonia. On heating, sodium metaphosphate is formed.

C. Pyrophosphoric Acid.

Exercise: Prepare a 10 per cent. aqueous solution of pyrophosphoric acid.

Operation: Heat 20 to 30 grams of disodium phosphate, with constant stirring, in a porcelain dish over a wire gauze, until the salt has again become solid. Fill a platinum crucible half full of the dry salt and heat it first over a Bunsen burner and then over the blast lamp. Care must be taken that the point of the flame of the blast lamp, and not the reducing portion, comes in contact with the crucible.¹ The heating is to be continued until no more gas bubbles are given off from the fused mass.

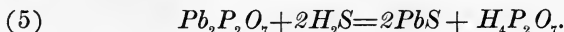


¹ Otherwise the platinum easily becomes brittle.

After cooling, dissolve the contents of the crucible in ten times their weight of water, and add a concentrated solution of lead acetate,¹ corresponding to the equation :



Filter off the precipitated lead salt, wash first with water and then with alcohol,² until no more lead can be detected in the filtrate. After it is dry, powder the lead pyrophosphate and cover it with sufficient water to yield a 10 per cent. solution of pyrophosphoric acid. Hydrogen sulfid is then led into the solution until the white lead salt is completely converted into black lead sulfid:



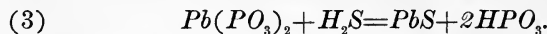
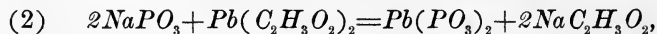
The solution of pyrophosphoric acid after filtration is placed in a dessicator over lime until the odor of hydrogen sulfid has completely disappeared.

Properties : The solution cannot be concentrated by evaporation, since by this the pyrophosphoric acid changes over into orthophosphoric acid. Silver nitrate gives a *white pulverulent* precipitate (distinction from orthophosphoric acid); albumen is not coagulated (distinction from metaphosphoric acid.)

D. Metaphosphoric Acid.

Exercise : Prepare a 10 per cent. aqueous solution of metaphosphoric acid.

This preparation is made from microcosmic salt in the same way as pyrophosphoric acid from disodium phosphate. The equations are:



¹ 1 part of water at 40° dissolves 1 part of $Pb(C_2H_3O_2)_2$ 3 aq.

² Lead acetate and sodium acetate are soluble in alcohol; lead pyrophosphate is insoluble in alcohol.

Properties : This solution cannot be concentrated by evaporation owing to the fact that metaphosphoric acid is gradually changed into pyrophosphoric acid. Silver nitrate gives a white gelatinous precipitate. The aqueous solution of metaphosphoric acid coagulates albumen solution (distinction from ortho- and pyro-phosphoric acid.)

14. Lead Peroxid.

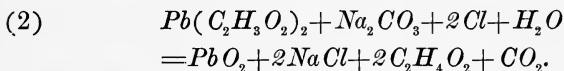
(Intermediate Product : *Lead Acetate.*)

Raw Materials : Lead oxid (litharge), glacial acetic acid, soda, common salt, manganese dioxid, concentrated sulfuric acid, dilute nitric acid.

Acetic acid converts litharge into lead acetate (sugar of lead) according to the equation :



If the solution of lead acetate is treated with soda, and chlorin led into the mixture, lead peroxid is formed :



Exercise : Convert 100 grams of litharge into lead acetate, and from 100 grams of this product prepare lead dioxid.

Operation : a. Preparation of lead acetate. Use 100 grams of the litharge¹ obtained as a by-product in Preparation 11. Cover the litharge in a porcelain dish with the amount of 33 per cent. acetic acid² required by equation (1), and heat to boiling. As soon as the litharge is dissolved, filter through a hot

¹ This litharge is usually contaminated with iron oxid and lead carbonate. If the latter is present there will be effervescence on the addition of acetic acid.

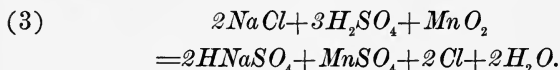
² One part of glacial acetic acid and two parts water.

water funnel. It may be found necessary to add somewhat more acetic acid to complete the solution. On cooling, the solution solidifies to a crystalline mass of fine needles. Drain off the brown mother liquor (why brown?) with a filter pump, and dry the crystals between filter paper. The product, known as sugar of lead, has the composition $Pb(C_2H_3O_2)_2 \cdot 3aq.$

b. Preparation of lead dioxid. Dissolve in water, each by itself, 100 grams of sugar of lead, and the quantity of soda required by equation (2). Mix the solutions in a liter flask and lead chlorin into the mass through a glass tube which reaches to the bottom of the glass. Continue the current of chlorin until the white carbonate is completely converted into the brown peroxid.

To prepare the chlorin, place in a flask an intimate mixture of two parts finely powdered pyrolusite (MnO_2) and two parts salt, and add a cooled mixture of six parts concentrated sulfuric acid with two parts water.

This corresponds, when the the pyrolusite contains 70 per cent. MnO_2 , approximately to the equation :



The evolution of chlorin begins in the cold, but should be assisted by *gentle* warming of the flask on a sand bath. By careful regulation of the temperature a steady stream of chlorin is obtained.

A wash bottle (*B* Fig. 1) with water should be placed between the flask in which the chlorin is evolved and the vessel in which the lead peroxid is formed. At the beginning of the reaction more or less chlorin escapes unused, hence the materials used for the evolution of chlorin must be in excess of the theoretical quantity; usually one-third more than is required by equation (2) will be sufficient. After the operation, which requires about $1\frac{1}{2}$ hours, is ended the contents of the flask containing the lead peroxid are warmed on the water bath, poured into a

beaker glass, and the clear supernatant liquid decanted. The lead peroxid is then digested in the beaker glass with dilute nitric acid, in order to dissolve out any undecomposed lead carbonate; after repeated decantations with warm water it is filtered and washed until the wash-water ceases to show an acid reaction.

Yield : 62 to 65 grams lead peroxid, in place of ? grams required by theory.

Properties and Tests : Dark brown amorphous powder, insoluble in nitric acid. The product should lose no lead by digestion with nitric acid, but should dissolve to a clear solution in nitric acid on the addition of potassium nitrite.

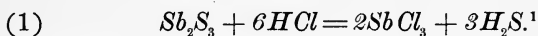
15. Antimony Trichlorid $SbCl_3$.

(**By-product :** *Sodium Sulfid*, Na_2S .)

Raw Materials : Floated stibnite, concentrated hydrochloric acid, caustic soda.

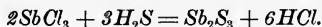
The decomposition of stibnite by hydrochloric acid is dependent upon the concentration of the acid and the temperature of the reaction.

Hydrochloric acid containing 25 per cent. HCl or more, decomposes stibnite slowly, even in the cold, but more rapidly on heating:



Exercise : *Convert 100 grams of stibnite into antimony tri-*

¹ This is a reversible reaction. From solutions of antimony trichlorid in dilute hydrochloric acid, hydrogen sulfid precipitates antimony sulfid:



If the strength of the hydrochloric acid be such that the acid decomposes the antimony sulfid when hot but not when cold, then the clear hot solution is apt to precipitate the red antimony sulfid on cooling, unless the hydrogen sulfid has been completely boiled out of the solution.

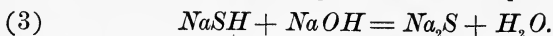
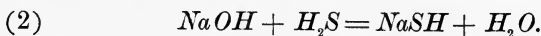
chlorid, and obtain as a by-product 1 liter of 5 per cent. aqueous solution of sodium sulfid.

Operation: Dissolve in 800 cc water the quantity of caustic soda required by equations (2) and (3); divide the solution into two equal portions and place one in the retort *C* (Fig. 1, page 4); the wash bottle *B* contains water. The finely powdered (floated) stibnite is placed in the flask *A* and about twice the quantity of concentrated hydrochloric acid added, which is required by the equation (1). (Why is more than the theoretical quantity required?) The decomposition is aided by a gradually increasing heat, and is complete when the evolution of gas ceases.

Time of Operation: About 2 hours.

If the stibnite contains compounds of arsenic, the easily volatile arsenious chlorid, $AsCl_3$, passes over with the steam into the wash bottle, where arsenious sulfid will be precipitated.¹

The retort will now contain a solution of sodium hydrosulfid, and to this the reserved portion of sodium hydroxid is added. The retort is then rinsed with sufficient water to make the solution up to 1 liter.²



After the undissolved sand, etc., in the flask has completely settled to the bottom, the solution is poured from the deposit into a tubulated retort (*A*, Fig. 11), a thermometer inserted in the tubulature, and the larger portion of the water and hydrochloric acid distilled over into receiver *B*. The tubulature *b* contains a tube *c* to lead away the hydrochloric acid fumes. When the thermometer reaches 120° the liquid contents of the retort are transferred to a distillation flask (*A*, Fig. 12) and submitted to

¹ This behavior should be noticed. If iron sulfid contains arsenic, the hydrogen sulfid made from it is liable to contain arsenic. This is of especial importance in forensic work.

² The solution of sodium sulfid is to be preserved for Preparation 18.

fractional distillation. The portion distilling below 180° , and that from this point up to 220° , are collected separately and the distillate is then tested by letting a drop fall on a watch glass to see if it solidifies. If this is the case, the receiver *B* is to be again changed and the distillation continued so long as anything passes over. *Care must be used* to see that the distillation tube does not become stopped by solidified antimony trichlorid; should this happen the mass is to be melted by the flame. In the retort there remains a brownish-yellow residue of basic iron chlorid, derived from the iron contained in the stibnite. The distil-

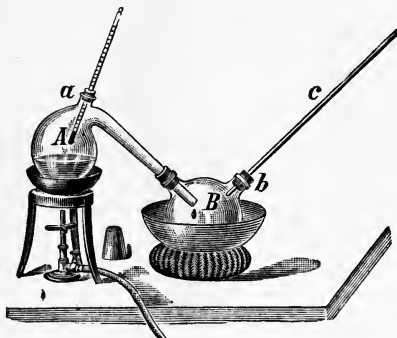


Fig. 11. Concentration of Antimony Trichlorid.

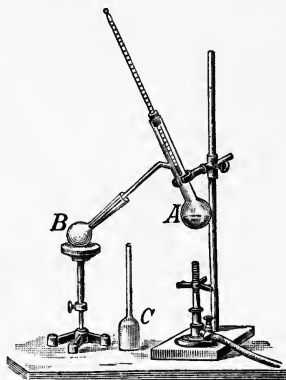


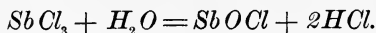
Fig. 12. Fractional Distillation of Antimony Trichlorid.

lates are generally somewhat yellowish in color from iron chlorid carried over. From the liquid portions which passed over first further quantities of the solid product may be obtained by repeated fractional distillations; by finally redistilling the united solid products a colorless preparation is obtained, solidifying to a crystalline mass. This is preserved in a flask (*C*, Fig. 12) whose tubular neck can be sealed by fusing.

The yield cannot correspond to the theoretical, because antimony trichlorid is somewhat volatile with superheated steam

and therefore it passes over into the latter portions of the aqueous distillate; the yield depends further upon the purity of the stibnite.

Properties: Antimony trichlorid forms a white crystalline mass, melting at 73° and boiling at 221° . It deliquesces gradually in the air, absorbing moisture; it is miscible with small quantities of water, but with larger amounts it is decomposed into antimony oxychlorid and hydrochloric acid.

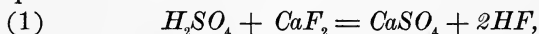


16. Fluosilicic Acid.

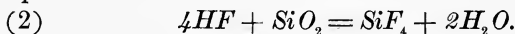


(By-product: *Silicic acid.*)

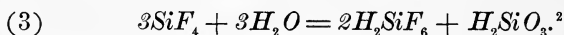
Raw Materials: Calcium fluorid (fluorspar), silicic acid (kieselguhr [infusorial earth], or quartz sand),¹ concentrated sulfuric acid, (about 1 kilo of mercury). The hydrofluoric acid liberated by the action of concentrated sulfuric acid on fluor-spar:



reacts upon silicic acid present in the mixture according to the equation:

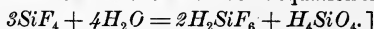


The water is retained by the excess of concentrated acid present, while the silicon tetrafluorid is led into water, where it is immediately decomposed into gelatinous silicic acid which is precipitated, and fluosilicic acid.



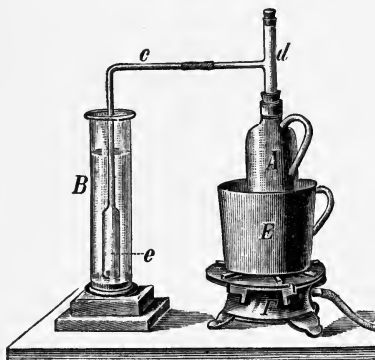
¹ The silicic acid obtained as a by-product in a previous preparation can be used.

[² Prof. T. H. Norton has shown that this equation should probably be :



Exercise: *Convert the calcium fluorid obtained as a by-product from the preparation of alumina and soda from cryolite (page 16), or 100 grams of fluorspar, into fluosilicic acid.*

The **Apparatus** (Fig. 13) used consists of the vessel *A* and the glass cylinder *B*, holding about a liter, which are connected by the tubes *c* and *d*. As a vessel for the evolution of SiF_4 a stone mineral water bottle holding about $\frac{3}{4}$ liter answers well. This bottle stands in an iron pot surrounded by sand, which serves as a sand bath, and the pot rests upon a



No. 13. Prep'n of Fluosilicic Acid.

Fletcher burner *F*. The T-tube *d* should be as large as possible, and is fitted into the bottle by a cork or by plaster of Paris. The lower opening of the tube should have a hole filed in the side, and the upper opening is closed by a cork. This cork should fit rather loosely, so that if the tube *c e* becomes stopped, it can act as a safety valve. The glass tube *c* with its enlarged end *e* reaches to the bottom of the glass cylinder *B*.

Besides the above there are necessary, a strainer (Fig. 4, page 17) of flannel,¹ and a glass spoon, which can be made before the blast lamp. A ball is blown on the end of a glass tube, and then having softened one side of the ball in the flame, the air is rapidly sucked out.

Operation : The silica is advantageously used in a very finely divided condition, such as kieselguhr or infusorial earth, and one-fourth more should be used than is theoretically required. (If quartz sand is used double the quantity should be taken.) The sulfuric acid must be in large excess (why?); to 100 grams of calcium fluorid use at least 500 grams sulfuric acid. The calcium fluorid and the silicic acid should be previously heated

¹ When the liquid is acid, the cloth for the strainer should be of animal fibre (wool), when alkaline, of vegetable fibre (cotton or linen), (compare Preparation 6, page 16.)

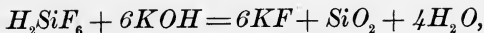
in an iron dish until every trace of moisture is expelled, and every trace of organic matter in the kieselguhr is destroyed. After cooling they are to be finely ground in a mortar, intimately mixed, and then poured into the bottle. The apparatus is then set up, great care being taken that the interior of the tubes *c* and *d* is quite dry. Into the glass cylinder pour enough mercury to just close the opening of the tube *c* and then fill the cylinder four-fifths full of water. Pour the sulfuric acid into the bottle through the **T**-tube by means of a long-necked funnel, close the opening of the **T**-tube and light the flame under the sand bath. The evolution of gas begins immediately¹ and is easily controlled. After the air has been expelled, the ascending bubbles become covered with a film of silicic acid. This collects at first at the surface as a gelatinous mass and gradually fills the cylinder. When the contents of the cylinder become so thick that the gas bubbles find their way to the surface with difficulty, portions should be removed to the strainer with the glass spoon, and fresh portions of water added. Toward the end of the reaction, which may be recognized by the slower evolution of gas, tubes of silicic acid are generally formed from the surface of the mercury, and through these the gas ascends undecomposed.

Time of Operation : 2 to 3 hours.

The contents of the cylinder are now poured off from the mercury on to the strainer and thoroughly washed. The silicic acid is then squeezed out, removed from the strainer and dried. The percolate is clarified by filtering through paper.

The estimation of the strength of the solution in fluosilicic acid is best determined by titration with normal alkali at a boiling temperature, litmus being used as an indicator.

¹ If the calcium fluorid was not thoroughly washed, sodium carbonate will be present, owing to the decomposition of the aluminate by the carbon dioxid of the air. In this case carbon dioxid will be evolved.



1 cc normal alkali corresponds to 0.024 gram H_2SiF_6 .

The yield is about 80 per cent. of the theoretical.

Properties : Fluosilicic acid cannot be concentrated by evaporation, since it is gradually decomposed into silicon tetrafluorid and hydrofluoric acid. In not too dilute solutions, sodium and potassium hydroxids produce colorless translucent precipitates of sodium and potassium fluosilicates. Barium fluosilicate is insoluble even in hydrochloric acid, but is easily distinguished from barium sulfate by its crystalline structure when seen under the microscope.

17. Crystallized Silicon.

(Intermediate Product : *Potassium Fluosilicate.*)

Raw Materials : Fluosilicic acid, potassium hydroxid, aluminum filings, hydrochloric acid.

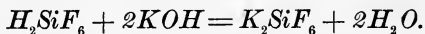
On heating potassium fluosilicate with aluminum, silicon is obtained, together with potassium fluorid and aluminum fluorid:



If more aluminum is used than is required by the equation, the fused excess dissolves the silicon, and, on cooling, the latter separates out in small crystals.

Exercise : Obtain the silicon in the fluosilicic acid made in Preparation 16.

Operation : Neutralize the fluosilicic acid exactly with a concentrated solution of potassium hydroxid :



This is easily accomplished if one reserve a small portion of the acid to add to the balance when it has been neutralized.

The translucent, iridescent precipitate soon settles; after filtration by suction and drying, the potassium fluosilicate is obtained as a white amorphous powder.

This is next ground very intimately with one-third its weight of aluminum filings, placed in a Hessian crucible, covered with a further quantity of aluminum, and the whole then heated about a half hour at a red heat.

On breaking the crucible, a larger regulus is found, together with smaller masses of grayish color, on whose surface little shining silicon crystals can be seen, presenting generally under the lens the appearance of octaedra. These metallic masses are freed mechanically from the slag, and then treated with hydrochloric acid. The aluminum dissolves, leaving the silicon in grayish black, graphite like, shining crystal flakes.

Yield : About one-tenth of the potassium fluosilicate used (= ? per cent of theoretical product?)

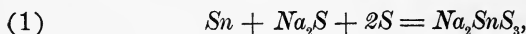
Properties : Crystallized silicon is not attacked by acids, but solutions of potassium and sodium hydroxids dissolve it with evolution of hydrogen and formation of silicates. It is harder than glass and does not burn when heated on platinum foil. It can be freed from any silica which may be mingled with it by treating with hydrofluoric acid in a platinum dish.

18. Recovery of Tin from Tin Plate.

(**Chief Product :** *Tin*; **Secondary Product :** *Potassium Cyanate.*)

Raw Materials : Scrap tin plate, sodium sulfid, flowers of sulfur, crude hydrochloric acid, potassium cyanid.

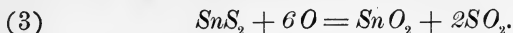
Tin plate contains 4 to 6 per cent. of tin, which can be separated from the iron by treatment with sodium sulfid and sulfur. Soluble sodium thio-stannate is formed:



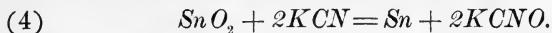
from which tin sulfid is precipitated by acids:



By roasting in the air, tin sulfid is oxidized to tin oxid:



By fusion with potassium cyanid, tin oxid is reduced to tin:



Exercise: *Recover the tin from one kilo of tin plate scrap.*

Operation: Place the tin scrap, cut into small pieces, in an iron vessel and add the theoretical quantity of sodium sulfid solution from Preparation 15, required for the formation of sodium thiostannate, assuming that the scrap contains 6 per cent. tin. Add the required quantity of flowers of sulfur and sufficient water to cover the scraps. Heat to boiling and continue the boiling with the addition of water from time to time to replace that lost by evaporation. In one or two hours all the tin should be removed from the iron. Cool and pour the yellow liquid from the iron, filter if necessary through a sand filter,¹ heat to boiling and precipitate with concentrated hydrochloric acid (crude). Strain the precipitated tin sulfid through flannel, squeeze and dry.² The tin sulfid is then spread in a thin layer upon an iron plate and roasted over a Bunsen burner. The operation is complete when a sample, heated in an open tube, gives off no fumes of sulfur. The tin oxid contains some sodium chlorid, which is now removed by boiling with water.

The reduction of the tin oxid is carried out best in a Hessian crucible in which the amount of potassium cyanid required by

¹ The filtrate is often colored greenish-black by the presence of a little Na_2S, Fe_2S_2 . This is, however, in no way detrimental in the subsequent operations.

² The voluminous precipitate is washed with difficulty. It is, therefore, easier to purify the roasted product. The tin sulfid is best dried by spreading out on porous tiles or bricks.

equation (4) has been fused. The thoroughly dried tin oxid is added little by little, the melt being from time to time stirred with an iron rod, and finally heated until the contents have come to a quiet fusion.

After cooling, the crucible is broken, the regulus of tin separated from the slag (potassium cyanate), and the latter saved for the following preparation.

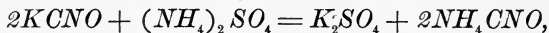
Yield: 30 to 40 grams of tin.

19. Carbamid (Urea).

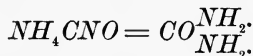


Raw Materials: Potassium cyanate, dilute sulfuric acid, ammonia, alcohol.

Potassium cyanate reacts with ammonium sulfate, forming potassium sulfate and ammonium cyanate:



and ammonium cyanate in aqueous solution undergoes when heated an intermolecular change into carbamid:



Exercise: Convert the potassium cyanate obtained as a by-product in Preparation 18 into urea.

Operation: Boil the slag from the tin regulus and the crucible with a solution of ammonium sulfate, filter and evaporate the filtrate to dryness in a porcelain dish on a water bath. The ammonium sulfate is prepared by neutralizing with ammonia the quantity of sulfuric acid corresponding to the potassium cyanid used in Preparation 18.

The separation of the urea from the potassium sulfate (and from any excess of ammonium sulfate present) is accomplished

by boiling the residue with alcohol in a reflux condenser. (Fig. 14.) The round-bottomed flask *A*, which contains the residue

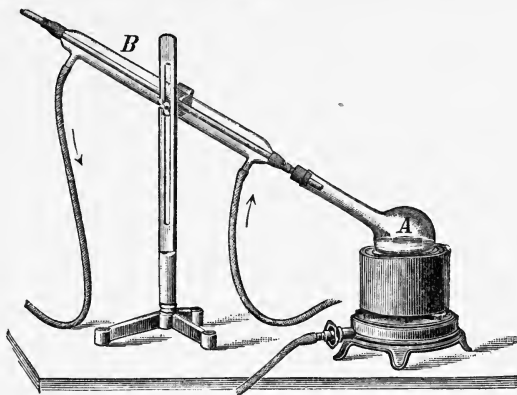


Fig. 14. Heating with a Reflux Condenser.

and about 0.25*l* alcohol (sp. gr. 0.82), is connected with the cooler *B* and heated on a water bath. After the boiling of the alcohol has continued for half an hour, the flame under the water bath is extinguished, the flask detached from

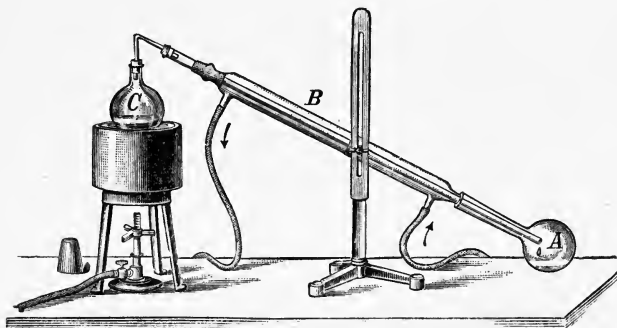


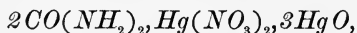
Fig. 15. Distillation of the Alcohol.

the cooler and the solution filtered into a short-necked flask, *C*. Care should be used that the undissolved matter which settles

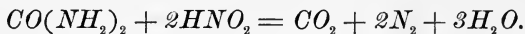
rapidly to the bottom of the flask is not poured out on the filter. The flask *C* is then connected by a tube bent at an acute angle with the cooler (Fig. 15) and the flask containing the residue is used as a receiver at the lower end of the condenser. The alcohol is distilled off until only a few cubic centimeters remain. This solution is poured into a small crystallizing dish. On cooling, the urea crystallizes in flat prisms. Repeat the extraction of the residue in the flask with the distillate until no more urea is obtained. Two extractions usually suffice.

Yield: 30 to 40 grams of urea from 60 grams potassium cyanid, instead of ? grams theoretical.

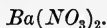
Properties of Urea: Melts on platinum foil and decomposes on further heating, leaving no residue. Easily soluble in alcohol, more soluble in water. From the aqueous solution, nitric acid precipitates urea nitrate, $CO(NH_2)_2, HNO_3$, which is difficultly soluble, especially in nitric acid. With mercuric nitrate an insoluble compound is formed,



which is used for determination of urea by Liebig's method. On treatment with sodium hypobromite, $NaOBr$, (Knop-Hüfner method of determining urea) or nitrous acid, carbamid is decomposed into carbon dioxid and nitrogen:



20. Barium Nitrate.



Raw Materials: Powdered heavy spar (barite), charcoal powder, nitric acid.

Barium sulfate is decomposed by carbon at a red heat:



Barium sulfid is formed which dissolved in nitric acid with the formation of barium nitrate:



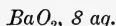
Exercise : *Convert 100 grams of barite into barium nitrate.*

Operation : A mixture of powdered barite and very finely powdered charcoal, in the proportions given by equation (1), is ground together very thoroughly and heated to redness in a Hessian crucible about an hour. On cooling, the contents of the crucible should form a reddish grey, porous, friable mass.¹ This is then pulverized and added in small portions to the nitric acid required by equation (2). The nitric acid should be diluted with sufficient water to dissolve in the cold all the barium nitrate formed. At this dilution very little of the evolved hydrogen sulfid is oxidized to sulfuric acid, hence there will be no re-formation of barium sulfate. When all the barium sulfid has been added to the nitric acid, the hydrogen sulfid is expelled by heat, the solution filtered, and evaporated to crystallization. A second crop of crystals is obtained on further evaporation and the rest of the salt can be precipitated by alcohol.

Yield : 80 to 90 per cent. of the theoretical.

Properties: White, brilliant octaedra, insoluble in alcohol.

21. Hydrated Barium Peroxid.



(Intermediate Product : *Barium Oxid.*)

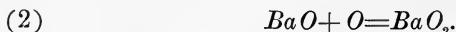
Raw Materials : Barium nitrate, barium hydroxid, hydrochloric acid, ice.

¹ If the contents of the crucible are still pulverulent they must be ground again and heated a second time.

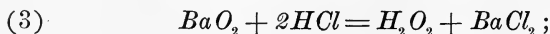
When barium nitrate is heated to redness, barium oxid is formed:



when a current of air is led over the barium oxid, the peroxid is formed:



If barium peroxid is treated carefully with hydrochloric acid in the cold, an aqueous solution of hydrogen peroxid is formed:



crystalline hydrated peroxid of barium is precipitated on the addition of baryta water to this solution of hydrogen peroxid:



Exercise: *Convert the barium nitrate obtained in Preparation 20 into hydrated barium peroxid.*

Operation: The barium nitrate is gradually heated in a Hessian crucible until it reaches a low red heat. On cooling, the contents of the crucible appear as a greenish gray, hard, porous mass, which can generally be separated from the walls of the crucible only by breaking it. This mass should be immediately placed in tight, dry receptacles, to prevent its absorption of moisture from the atmosphere. A small sample should be tested by heating in a hard glass tube, and in case brown gases are given off, the whole quantity must be reheated in a crucible.

To prepare the barium peroxid, a hard glass tube¹ of 1.5 cm diameter is filled with pieces of barium oxid the size of peas, each end is loosely closed with a wad of asbestos and fitted with a cork containing a glass tube to which a rubber tube is attached. All the fittings should be air tight. The tube is then

¹ The length of the tube depends upon the length of the combustion furnace used. After filling, the tube is to be weighed.

heated in a combustion furnace to a dull red heat,¹ while a current of air is led through it. In order to be able to judge of the rapidity of the air current, a wash bottle containing concentrated sulfuric acid should be placed at the end of the tube into which the air enters.

The simplest method of leading the air through the tube is by the use of a two-flask (Muencke) aspirator, or a filter pump.

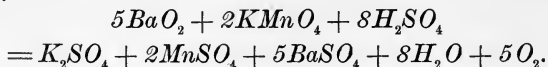
5 liters air correspond to about 1 liter oxygen.

When the tube has been cooled it is weighed ; the operation, which requires two to three hours, is to be considered finished when the increase in weight corresponds approximately to the theory.

The amount of hydrochloric acid corresponding to equation (3) is now diluted with water until its strength is 1 or 2 per cent., and is cooled by the addition of ice. The powdered barium peroxid is added in small portions. The temperature of the solution should be kept at 0° by further quantities of ice. If all the barium peroxid does not dissolve, any deposit is to be rubbed in a porcelain mortar with repeated portions of the solution, or, if necessary, with the addition of small quantities of dilute hydrochloric acid, until no more dissolves. The united acid solutions are now neutralized with a solution of barium hydroxid (baryta water), or even made very slightly alkaline, the impurities (alumina, iron oxid from the crucible) being as a result precipitated. The solution is then filtered, and by further addition of baryta water, hydrated barium peroxid is precipitated. This is filtered, washed and preserved in a moist condition (*en pâte*).

¹ At a dull red heat barium oxid absorbs oxygen from the air (equation (2)); at a bright red heat the reverse reaction takes place, in which barium peroxid is decomposed into barium oxid and oxygen, ($BaO_2 = BaO + O$). The technical method of obtaining oxygen from the air depends upon these reactions.

The yield is determined by titration with potassium permanganate:



Properties : Brilliant quadratic flakes; insoluble in water; decomposed on standing (even in a moist condition) into barium hydroxid and oxygen. If a few crystals are dissolved in dilute hydrochloric acid, covered with ether, and then a trace of potassium chromate is added, perchromic acid is formed, which, when the solution is shaken with the ether, imparts to it a violet color.

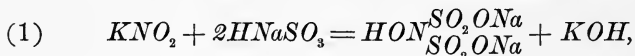
22. Hydroxylamin Hydrochlorid,¹



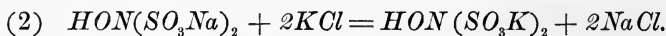
(Intermediate Product: *Potassium Hydroxylamin Disulfonate* [sulfazotate].)

Raw Materials: Soda, concentrated sulfuric acid, potassium nitrite, potassium chlorid, barium chlorid, alcohol, charcoal, ice.

If one molecule of potassium nitrite reacts at a temperature of 0° with two molecules of hydrogen sodium sulfite,² there is formed the sodium salt of hydroxylamin disulfonic acid:



and this in turn reacts with potassium chlorid to form the difficultly soluble potassium salt:

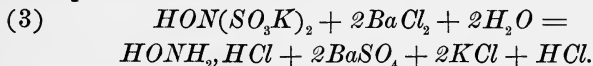


If the aqueous solution of the potassium hydroxylamin disul-

¹ Discovered by W. Lossen in 1865, and first prepared from ethyl nitrite.

² According to F. Raschig (D. R. Patent 41,987.)

fonate is boiled with barium chlorid, the following reaction takes place:



The hydroxylamin hydrochlorid can be separated from the potassium chlorid by alcohol, in which the former is soluble and the latter insoluble.

Exercise: *Convert 106 grams of calcined soda into hydrogen sodium sulfite and use a solution of the latter to prepare the hydroxylamin hydrochlorid.*

Operation: Into a cold saturated solution of soda, lead a rapid current of sulfur dioxid until a portion of the solution, even after shaking, still smells strongly of sulfur dioxid.

Time of Operation: 2 to 3 hours.



For the preparation of sulfur dioxid fill a round-bottomed liter flask to the neck with coarse pieces of dried charcoal; add concentrated sulfuric acid until the flask is half full, and heat on a sand bath (apparatus as in Fig. 1).



Dissolve the amount of potassium nitrite required by equation (1) in 0.5 liter of water, cool the solution and also that of the hydrogen sodium sulfite to 0° , by adding pieces of ice. Now surround the flask containing the potassium nitrite solution with broken ice, and add the sulfite solution little by little, so slowly that the temperature of the mixture does not rise appreciably above 0° . Make a cold saturated solution of the amount of potassium chlorid required to decompose the sodium salt according to equation (2), cool with ice, add to the mixture, and let the whole stand over night. The next morning filter off the solid crystalline crusts of hydroxylamin disulfonate of potassium which have separated out, and after drying on filter paper, weigh. (The

yield should be upwards of 80 per cent. of that theoretically possible.)

To convert this salt into hydroxylamin hydrochlorid, dissolve it in five times its weight of hot water, add the requisite quantity of barium chlorid, according to equation (3), in hot saturated solution, and heat the mixture for an hour to its boiling point. If the solution still contains sulfuric acid, barium chlorid is added until a filtered test shows no further precipitate. Filter off the barium sulfate, evaporate on the water bath to dryness and extract the residue repeatedly with 0.25 liter of alcohol, as in the case of urea (see page 50).

Yield: 20 to 30 grams of hydroxylamin hydrochlorid.

Properties of Hydroxylamin Hydrochlorid: Crystallizes from water in flakes, from alcohol in monoclinic crystals. It is decomposed on heating on a platinum foil, leaving no residue. The aqueous solution acts as a strong reducing agent in the presence of an alkali. By the reduction of copper salts (compare page 20) as little as 1 part in 10,000 of hydroxylamin may be detected. (Lossen.)

23. Phosphorus Pentachlorid.



Raw Materials : Red phosphorus, common salt, pyrolusite, concentrated sulfuric acid. Chlorin reacts upon red phosphorus when heated with the formation of phosphorus pentachlorid:



Exercise : Convert 20 grams of red phosphorus into phosphorus pentachlorid.

Apparatus : The chlorin is evolved in a round-bottomed 2 liter flask;

this is connected with a wash bottle (Fig. 1, *A* and *B*) containing concentrated sulfuric acid, and in order to dry the chlorin thoroughly, the wash

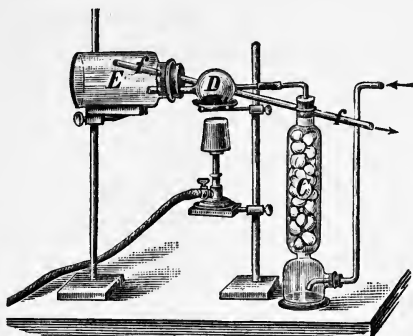


Fig. 16. Prep. of Phosphorus Pentachlorid.

bottle is in turn connected with a U-tube or a scrubber (*C* in Fig. 16) filled with pieces of pumice stone saturated with concentrated sulfuric acid. The phosphorus is placed in a bulbed tube *D*, which is formed by fusing a glass tube on to the bottom of a round-bottomed 200 cc flask. The bulb of the tube rests upon a small sand bath. The neck of the flask should be 15 to 20 mm wide, but as short as possible, and it projects through a cork stopper into the wide-mouthed bottle *E*, which serves as a receiver. The cork is also pierced by a glass tube *f*, from 30 to 40 cm long and large enough to be easily cleared out by a glass rod in case it becomes stopped up. The arrangement of the bulbed tube and receiver is shown in the figure. The stopper is saturated with melted paraffin, and need not close the bottle tightly. The apparatus is placed under a good draught.

Operation : Place the thoroughly dried phosphorus in the bulbed tube *D*. Fill the flask for preparing chlorin as described in Preparation 14 (page 39), and use for this enough material to correspond to $1\frac{1}{2}$ times the chlorin required by equation (1). With a small flame under the sand bath, regulate the temperature to correspond with the evolution of chlorin. At the beginning of the reaction, and in case the chlorin is not perfectly dry, hydrochloric acid and phosphorus oxychlorid are given off through the tube¹ *f*. Later the flame of the phosphorus burning in the stream of chlorin is seen. Occasionally, especially toward the end of the operation, the bulbed tube should be turned on its axis, in order to drive off the product

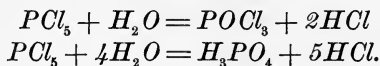
¹ Also arsenic trichlorid, if the phosphorus contains arsenic.

which has sublimed in the cooler parts of the tube. The impurities of the phosphorus which are not volatile with chlorine remain in the bulbous tube, and should be examined qualitatively. The phosphorus pentachloride which is deposited in the neck of the bulbous tube is easily scraped into the bottle.

Time of Operation : 2 to 3 hours.

Yield : 80 to 90 per cent. of the theoretical.

Properties : Slightly yellowish, crystalline mass, fuming in moist air, and decomposed by a little water into hydrochloric acid and phosphorus oxychloride, by much water into hydrochloric and phosphoric acids:



24. Monochlorosulfuric Acid.

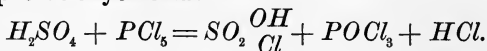


(Sulfuryl hydroxychloride.)

(Intermediate product: Anhydrous sulfuric acid.)

Raw Materials: Concentrated sulfuric acid, fuming sulfuric acid, phosphorus pentachloride.

If phosphorus pentachloride is added to anhydrous sulfuric acid, there is formed hydrochloric acid, monochlorosulfuric acid and phosphorus oxychloride:



The phosphorus oxychloride reacts further with sulfuric acid forming more monochlorosulfuric acid and metaphosphoric acid:



Exercise: Convert 200 grams of anhydrous sulfuric acid into monochlorosulfuric acid.

Operation: 1. Preparation of anhydrous acid (H_2SO_4). Determine by titration:

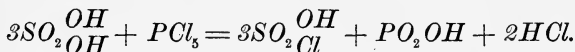
(a) The amount of H_2SO_4 and H_2O in the concentrated sulfuric acid;

(b) The amount of H_2SO_4 and SO_3 in the fuming sulfuric acid; and mix them in such proportion that H_2SO_4 will be formed:

$$(aH_2SO_4 + xH_2O) + \left(bH_2SO_4 + \frac{80}{18}xSO_3\right) = \left(a + b + \frac{98}{18}x\right)H_2SO_4.$$

2. Preparation of the chlorid. Pour the anhydrous sulfuric acid in a round-bottomed 1.5 liter flask, and add the calculated quantity of phosphorus pentachlorid slowly with a porcelain spatula.

The equation to be used is:



The reaction is violent. (Time of operation $\frac{1}{2}$ hour.) After the phosphorus pentachlorid has all been added, warm the flask upon a sand bath until no more hydrochloric acid escapes, then pour the product into a tubulated retort (A, Fig. 11) and distill the monochlorosulfuric acid over a sand bath. The tubulated receiver should be perfectly dry, and should be so fitted on the retort that the distillate falls freely into it. When the thermometer reaches 160° the distillation is stopped. The residue in the retort consists of metaphosphoric acid and undecomposed sulfuric acid. The distillate should be redistilled from a distilling flask fitted to a condenser (Fig. 12) and should be preserved in a dry, glass-stoppered bottle.

Yield: About 80 per cent. of the theoretical quantity.

Properties: Boiling point 153° . Fumes in moist air and decomposes gradually into sulfuric acid and hydrochloric acid; on dropping it into water, decomposition takes place with explosive violence.

25. Amidosulfonic Acid.



(Sulfaminic Acid.)

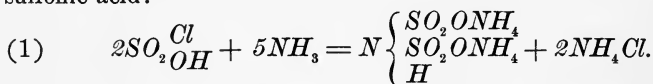
A. From Monochlorosulfuric Acid.

(Intermediate Product: Barium imidosulfonate.)

Raw materials: Monochlorosulfuric acid, ammonia gas, barium chlorid, lime, caustic soda, chloroform, glycerol.

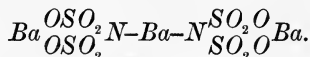
Exercise: Convert the sulfuryl hydroxychlorid¹ obtained in Preparation 24 into sulfaminic acid.

By the action of dry ammonia gas in the cold there is chiefly² formed beside ammonium chlorid, the ammonium salt of imidosulfonic acid:



Ammonium imidosulfonate is quite soluble in water and cannot be separated from ammonium chlorid by crystallization.

On adding a sufficient quantity of barium chlorid to the ammoniacal solution, the basic barium salt is formed, in which the imido-hydrogen also is replaced by barium:



This salt is insoluble in water and is thus readily separated from the ammonium chlorid.

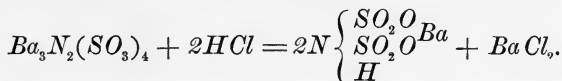
¹ Generally about 130 grams of sulfuryl hydroxychlorid will be obtained in Preparation 24; not less than 100 grams should be used.

² There is also formed, especially if the ammonia is not quite dry, more or less sulfuric acid:

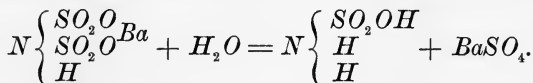


The sulfuric acid, as well as the imidosulfonic acid, unites with the excess of ammonia present to form the ammonium salt. Free imidosulfonic acid is not known.

On treating the basic barium salt with a little dilute hydrochloric acid, the crystalline neutral barium salt is formed:



On boiling with water this is decomposed into sulfaminic acid and barium sulfate:



Apparatus: The flask for preparing ammonia is connected with a wash bottle (*A* and *B*, Fig. 1) and this with two scrubbers (*C* and *D*, Fig. 17), one of which, *C*, is filled with pieces of lime the size of marbles, and the other, *D*, with short sticks of caustic soda. From *D* the dry ammonia passes through the T-tube *f*, which can be easily pushed up or down, and whose upper opening is closed by a cork, into the flask *E*, which holds from one to two liters. This flask is connected with an upright condenser (*B*, Fig. 14) which enters the enlarged opening (Fig. 17) of the bent tube *g*.

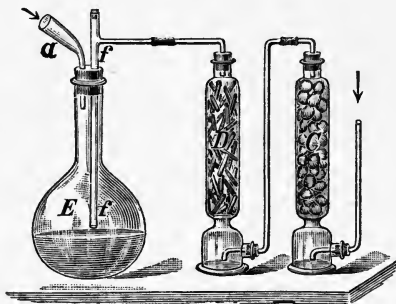


Fig. 17. Prep. of Amidosulfonic Acid.

Operation: Mix the sulfuryl hydroxychlorid with $2\frac{1}{2}$ its volume of chloroform dried over calcium chlorid, and pour the mixture into the flask *E*. Ammonia gas may be prepared as in Preparation 2, or more conveniently by gently warming concentrated ammonia. The gas must be in a completely dry condition when it enters *E*. With the apparatus described, a rapid stream of ammonia can be dried, if glycerol is used in the wash bottle, so that no moisture shall be carried over from this. At first the T-tube is given the position shown in Fig.

17, that is, its opening is just above the surface of the liquid; later when there is less danger of its becoming stopped up, it may enter the liquid.

Ammonium imidosulfonate formed on leading ammonia into sulfuryl hydroxychlorid, is insoluble in chloroform, and separates out, together with the ammonium chlorid. If the T-tube or the cooler become stopped, they can be easily opened by a glass rod.

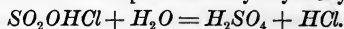
The mixture becomes heated by the reaction and the chloroform which passes off is condensed in the cooler, dropping back into the flask *E*. The completion of the reaction is indicated by the contents of the flask becoming cold, and smelling distinctly of ammonia after standing.

Time of Operation: 3 hours.

Filter off the chloroform from the solid residue, free it from ammonia by shaking with water in a separating funnel, and purify by distillation¹ on a water bath (Fig. 15.) A small portion of the residue on the filter paper should be dissolved in water as a test. If heat is generated, or if the solution has an acid reaction,² the whole residue must be replaced in the flask and ammonia led in again, without connecting with a condenser, until an average sample, rubbed thoroughly with water in a mortar, dissolves with alkaline reaction. The dry white powder (ammonium imidosulfonate and ammonium chlorid) is dissolved in the flask in *cold* water, the solution weakly acidified with hydrochloric acid, and a cold saturated solution of so much barium chlorid added as corresponds to $1\frac{1}{2}$ times the weight of sulfuryl hydroxychlorid used. The solution is then filtered from the precipitated barium sulfate into a vessel containing sufficient dilute ammonia to keep the filtrate alkaline; basic barium imido-

¹ In this way $\frac{2}{3}$ of the chloroform used may be readily recovered.

² This is the case if undecomposed sulfuryl hydroxychlorid is present:

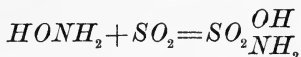


sulfonate then separates out. This is filtered off, freed as far as possible from moisture by pressure between filter paper, and suspended in water. To this barium salt, suspended in as little water as possible, add quickly just enough (not more!) dilute hydrochloric acid for solution. The walls of the vessel are then rubbed with a glass rod and almost immediately the neutral barium imidosulfonate ($NH(SO_3)_2Ba$) begins to crystallize out. When the precipitation is complete, the salt is filtered off and pressed between paper. To form the amidosulfonic acid, the neutral barium imidosulfonate is suspended in an equal quantity of water by weight, and the mixture warmed on the water bath (about half an hour) until a test shows no more crystals under the microscope. The barium sulfate is filtered off and the filtrate (without the wash water) set under a dessicator. In the course of one or two days the amidosulfonic acid separates out in beautiful crystals.

B. From Hydroxylamin.

Raw Material : Hydroxylamin hydrochlorid, sulfur dioxid.

Sulfur dioxid reacts upon an aqueous solution of hydroxylamin with the formation of amidosulfonic acid:

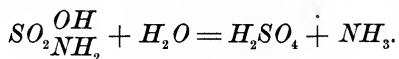


Exercise : *Convert the hydroxylamin hydrochlorid formed in Preparation 22 into amidosulfonic acid.*

Operation: Dissolve the hydroxylamin hydrochlorid in a small quantity of water, and lead sulfur dioxid into the solution for a long time (compare page 56). When the reaction is completed, the solution, on cooling, or after sufficient concentration on the water bath, deposits crystals of amidosulfonic acid. These are to be purified from the hydroxylamin, which clings to them very closely, by recrystallization.

Properties of Amidosulfonic Acid: Transparent, rhombic

crystals. The aqueous solution gives no precipitate with barium chlorid (distinction from sulfuric acid), and does not act as a reducing agent. When boiled with the addition of a mineral acid it is gradually decomposed with the formation of sulfuric acid and ammonia:



TABLES

Multiples of the Most Frequently Used Atomic Weights from One to Five.

(Rounded off to the whole numbers.)

		1	2	3	4	5
Aluminum	<i>Al</i>	27	54	81	108	135
Antimony	<i>Sb</i>	120	239	359	478	598
Barium	<i>Ba</i>	137	274	411	548	685
Calcium	<i>Ca</i>	40	80	120	160	200
Carbon	<i>C</i>	12	24	36	48	60
Chlorin	<i>Cl</i>	35	71	106	142	177
Copper	<i>Cu</i>	63	126	190	253	316
Fluorin	<i>F</i>	19	38	57	76	95
Iron	<i>Fe</i>	56	112	168	224	280
Lead	<i>Pb</i>	206	413	619	826	1032
Manganese	<i>Mn</i>	55	110	165	220	275
Nitrogen	<i>N</i>	14	28	42	56	70
Oxygen	<i>O</i>	16	32	48	64	80
Phosphorus	<i>P</i>	31	62	93	124	155
Potassium	<i>K</i>	39	78	117	156	195
Silicon	<i>Si</i>	28	56	85	113	141
Silver	<i>Ag</i>	108	215	323	431	538
Sodium	<i>Na</i>	23	46	69	92	115
Sulfur	<i>S</i>	32	64	96	128	160
Tin	<i>Sn</i>	118	236	354	472	590

Specific Gravity of Hydrochloric Acid.

(At 15° C.)

Sp. Gr.	Per Cent. HCl by weight.	Sp. Gr.	Per Cent. HCl by weight.
1.035	7.1	1.110	21.9
1.040	8.1	1.115	22.9
1.045	9.1	1.120	23.9
1.050	10.0	1.125	24.8
1.055	11.0	1.130	25.8
1.060	12.0	1.135	26.8
1.065	13.0	1.140	27.8
1.070	14.0	1.145	28.8
1.075	15.0	1.150	29.8
1.080	16.0	1.155	30.8
1.085	16.9	1.160	31.8
1.090	17.9	1.165	32.8
1.095	18.9	1.170	33.7
1.100	19.9	1.175	34.7
1.105	20.9	1.180	35.7

Specific Gravity of Nitric Acid.

(At 15° C.)

Sp. Gr.	Per Cent. HNO_3 by weight.	Sp. Gr.	Per Cent. HNO_3 by weight.
1.200	32.2	1.360	57.5
1.210	33.8	1.370	59.3
1.220	35.4	1.380	61.1
1.230	36.9	1.390	62.9
1.240	38.4	1.400	64.9
1.250	40.0	1.410	67.1
1.260	41.4	1.420	69.3
1.270	42.9	1.430	71.6
1.280	44.4	1.440	74.4
1.290	45.9	1.450	77.3
1.300	47.4	1.460	80.1
1.310	48.9	1.470	83.0
1.320	50.5	1.480	85.8
1.330	52.1	1.490	89.0
1.340	53.9	1.500	92.3
1.350	55.7	1.510	94.6

Specific Gravity of Concentrated Sulfuric Acid.

(At 15° C.)

Sp. Gr.	Per cent. H_2SO_4 by weight.
1.820.....	90.0
1.825.....	91.0
1.830.....	92.0
1.835.....	93.5
1.840.....	96.0

NOTE. The specific gravity of concentrated sulfuric acid increases until it reaches 1.8413 where it contains 97.7 per cent. H_2SO_4 . From this point the specific gravity decreases slightly, and there corresponds to

98.0	per cent. by weight H_2SO_4 ,	the specific gravity	1.8412
99.0	" " " "	" "	1.8403
100.0	" " " "	" "	1.8384

Specific Gravity of Ammonia.

(At 15° C.)

Sp. Gr.	Per Cent. NH_3 by weight.	Sp. Gr.	Per Cent. NH_3 by weight.
0.995	1.0	0.935	16.9
0.990	2.1	0.930	18.3
0.985	3.3	0.925	19.8
0.980	4.5	0.920	21.3
0.975	5.7	0.915	22.8
0.970	7.0	0.910	24.4
0.965	8.4	0.905	26.0
0.960	9.8	0.900	27.7
0.955	11.2	0.895	29.5
0.950	12.6	0.890	31.4
0.945	14.0	0.885	33.4
0.940	15.4	0.880	35.5

Solubility of Certain Salts in Water.

100 parts water dissolve ? grams.

At	0°	10°	20°	40°	60°	80°	100°
Alum $KAl(SO_4)_2, 12aq.$	3.9	9.5	15.1	30.9	66.6	134.5	357.5
Ammonium chlorid NH_4Cl	28.4	32.8	37.3	46.2	55.0	63.9	72.8
Barium chlorid $BaCl_2, 2aq.$	41.5	44.6	59.1	76.9
Barium hydroxid $Ba(OH)_2, 8aq.$	4.7	7.4	16.4	48.1	387.5	...
Barium Nitrate $Ba(NO_3)_2$	5.2	7.0	9.2	14.2	20.3	27.0	32.2
Copper sulfate $CuSO_4, 5aq.$	31.6	37.0	42.3	56.9	77.4	118.0	203.3
Ferrous sulfate $FeSO_4, 7aq.$	61	115 at 24°	227 at 46°	...	270 at 84°	...
Potassium chlorid KCl	28.5	32.0	34.7	40.1	45.5	51.0	56.6
Sodium carbonate (dehydrated) Na_2CO_3	12.6	21.4	38.1 at 30°	45.4
Sodium carbonate ¹ (crystallized) $Na_2CO_3, 10aq.$	21.3	40.9	92.8	273.6 at 30°
Sodium phosphate ² $HNa_2PO_4, 12aq.$	6.5	10.5	27.2	48.50

¹ Melts at 34° in its water of crystallization.² Melts at a little above 35° in its water of crystallization.

Solubility of Certain Salts in Water.

1 part substance requires for solution ? water.

At	0*	10°	20°	40°	60°	80°	100°
Alum <i>KAl(SO₄)₂aq.</i>	25.6	10.5	6.6	3.2	1.5	0.74	0.28
Ammonium chlorid <i>NH₄Cl</i>	3.5	3.0	2.7	2.2	1.8	1.6	1.4
Barium chlorid <i>BaCl₂aq.</i>	2.4	2.2	1.7	1.3
Barium hydroxid <i>Ba(OH)₂aq.</i>	21.3	13.5	6.1	2.1	0.026	...
Barium nitrate <i>Ba(NO₃)₂</i>	19.2	14.3	10.9	7.0	4.9	3.7	3.1
Copper Sulfate <i>CuSO₄aq.</i>	3.2	2.7	2.1	1.8	1.3	0.85	0.49
Ferrous sulfate <i>FeSO₄aq.</i>	1.6	0.87 at 24°	0.44 at 46°	...	0.37 at 84°	...
Potassium chlorid <i>KCl</i>	3.5	3.1	2.9	2.5	2.2	2.0	1.8
Sodium carbonate (dehydrated) <i>Na₂CO₃</i>	7.9	4.7	2.6 at 30°	2.2	2.2	2.2
Sodium carbonate (crystallized) <i>Na₂CO₃ 10aq.</i>	4.7	2.4	1.1	0.37 at 30°
Sodium phosphate <i>HNa₂PO₄ 12aq.</i>	15.4	9.5	3.7	0.021





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